

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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| In re Application of: | Robert E. Burgmeier, Richard Goodin, Joseph Delaney Jr. |
| Application No.: | 10/822581 |
| Filed: | April 12, 2004 |
| For: | Adhesion Technique for Incompatible Polymers Using Modified Polymer Tie Layers |
| Examiner: | Thao T. Tran |
| Group Art Unit: | 1794 |

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Docket No.: S63.2B-10865-US01

BRIEF ON APPEAL

This is a Brief on Appeal for the above-identified application in which Claims 1-7, and 10-11 were finally rejected in an Office Action mailed **March 17, 2008**. A Notice of Appeal, with a one month extension was filed on July 16, 2008.

This is the second Appeal Brief filed. The applicable fee is therefore believed to be \$10.00. The Commissioner is authorized to charge Deposit Account No. 22-0350 in the amount of \$10.00 along with any other fees which may be due.

(i) Real Party in Interest

The application is assigned to Boston Scientific Scimed, Inc., One SciMed Place, Maple Grove, MN 55311-1566, a Minnesota Corporation (former name Scimed Life Systems, Inc.). The assignee is a subsidiary of Boston Scientific Corporation, One Boston Scientific Place, Natick, Massachusetts, 01760-1537, a Delaware Corporation.

(ii) Related Appeals and Interferences

No related appeals or interferences are pending. This application was previously appealed (Notice of Appeal May 17, 2006; Appeal briefs filed July 17, 2006, November 16, 2006, January 3, 2007, March 8, 2007). Prosecution was reopened, without Examiner's Answer on July 13, 2007.

(iii) Status of claims

Claims 1-63 have been presented in this case. Claims 14-29 were previously withdrawn and have since been cancelled. Claims 4-6, 8-9 and 12-44 have also been cancelled. Claims 1-3, 7, 10-11 and 45-63 are pending. Currently pending claims 45-63 have been withdrawn. Claims 1-3, 7, 10-11 have been rejected. No claims have been allowed, or objected to. The claims that are being appealed are Claims 1-3, 7, 10-11.

(iv) Status of amendments

An Amendment After Final was filed May 1, 2008. An Advisory Action was mailed May 5, 2008 which stated the Amendment after Final would be entered for purposes of appeal. A Notice of Appeal, with a one month extension was filed on July 16, 2008.

In view of the statement in the May 5, 2008 Advisory Action, the claims stand in the form submitted in the May 1, 2008 Amendment After Final.

(v) Summary of claimed subject matter

According to independent claim 1, the invention is an article comprising a laminate having first and second layers and a tie-layer therebetween bonding the first and second layers, the first and second layers formed, respectively, of first and second polymer materials, the first and second polymer materials being different {pg 2, lines 5-15}, wherein

the first and second polymer materials, respectively, have first and second functional groups thereon {pg 11, lines 7-8}, and

the tie layer is formed of a tie-layer polymer material obtained by melt modification of one of the first or the second polymer materials {pg 2, lines 6-7}, said melt modification comprising incorporation therein of at least 5% by weight of a coupling agent {pg 3, lines 17-18}, the coupling agent having functional groups thereon, at least some of which are reactive in the melt with at least the functional groups on the other of said first and second polymer materials {pg 2, lines 13-14}, said coupling agent being selected from the group consisting of polyepoxides, polyoxazalines, polycarbodiimides, and polyisocyanates {pg 5, ln 14 - pg 6, ln 8}.

(vi) Grounds of Rejection to be Reviewed on Appeal

Review is sought of the rejection of claims 1-3, 7, 10-11 as obvious under 35

USC §103(a) from Wang et al, US 5,195,969, Samuelson et al, US 6,464,683, or Boer et al US

6,355,358, taken with Shimura et al, US 5,441,488.

(vii) Argument**A. The Invention**

The rejected claims pertain to laminate articles having a two layers of first and second polymer materials, respectively, and a tie-layer in-between the first and second polymer material layers. The tie layer is obtained by melt modifying one of the two polymer materials using a coupling agent that is reactive with functional groups on the other of the two polymer materials. The coupling agent is selected from the group consisting of polyepoxides, polyoxazalines, polycarbodiimides, and polyisocyanates. The laminates are particularly suited for medical device applications such as catheters and balloons.

B. The Examiner's Contentions

The full statement of the grounds for rejection as stated in the Final Action is reproduced below with emphasis added:

Wang teaches a laminate in a medical balloon or a catheter, the laminate comprising an innermost layer of polyethylene, an outermost layer of Nylon (polyamide), and a layer of Plexar sandwiched in between, Plexar is an anhydride-modified polyolefin, (See Figs 3-4; col. 4, ln. 14-15, 46-49)

Samuelson teaches a laminate in a medical tubing, the laminate comprising an outer layer 16, a core layer 12, and an intermediate tie layer 14 interposed between the outer layer and the core layer (see abstract; Fig. 1). The outer layer comprises a polyester or polyamide; the core layer comprises a polyethylene; and the intermediate tie layer comprises a polymeric material comprising functionality capable of adhering outer layer 16 to core layer 12, (See col. 6, ln. 5-6, 41-45, 57-59). The polymer of the intermediate tie layer comprises modified olefinic polymer having an anhydric moiety or maleic acid (see col. 7, ln. 12-51).

However, neither Wang [*sic.*] nor Samuelson teaches the amount of the modifying compound of the polyolefin or a catalyst in the intermediate layer.

Boer discloses an article comprising a thermoplastic multilayer composite. The multilayer composite has at least one layer I, at least one layer II, and an adhesion promoter (tie layer) disposed in between layer I and layer II (see abstract).

Boer further discloses that layer I comprises a polyamide molding composition. Layer II comprises a polyester molding composition (see col. 6, ln. 1-2) The adhesion promoter comprises at least 5% by weight of a graft copolymer prepared from the

following monomers: (a) a polyamine and (b) polyamide-forming monomers selected from lactams, aminocarboxylic acid, and/or equimolar combinations of diamine and dicarboxylic acid (see paragraph bridging col. 2-3), and 0.01-4.2 mol of an oligocarboxylic acid (see col. 4, ln. 8-13), *which appears to meet the requirement of the coupling agent in the presently claimed invention.*

The adhesion promoter layer in the invention of Boer further comprises polyamide and polyester (see paragraph bridging col. 7-8). The polymer composition in the adhesion promoter layer is crosslinked and a melt (see col. 5, ln. 22-44).

With respect to how the polymer is crosslinked, it has been within the skill in the art that how crosslinking of the polymer occurs would have no significant patentable weight.

The polyamide composition in layer I further contains up to 40% by weight of ethylene-propylene copolymers or aliphatic olefin copolymers (see col., 6, ln. 39-48).

Boer does not teach the use of an acid anhydride-modified polyolefin or a catalyst.

Shimura teaches a modified polyolefin as an adhesive in a laminate, the modified polyolefin comprising maleic anhydride is deposited on polyolefin or polyamide (see col. 4, ln. 51-56; col. 5, ln. 1-7). The content of acid anhydride is 0.5-50% (see col. 5, ln. 9-10).

The composition further comprises a catalyst, such as tertiary amine, to promote the reaction of the acid anhydride (see col. 5, ln. 40-43).

Therefore, it would have been obvious to one of ordinary skill in the art, at the time the invention was made, to have employed the modified polyolefin with the acid anhydride content and the catalyst, as taught by Shimura, in the tie layer of Wang, Samuelson, or Boer, for the purpose of enhancing adhesion between the tie layer and the outer and inner layer. This is because Shimura teaches that the use of such modified polyolefin and catalyst would have improved bonding and crosslinking between the modified polyolefin and polyamide or polyester

It is noted that in the prior art section of Boer, a catalyst is used in the adhesion promoter layer. Thus, it would have been obvious to one of ordinary skill in the art to have employed a catalyst in the adhesion promoter layer of Boer for the purpose of enhancing the efficacy of polymerization of the copolymer in the layer.

C. The Applicable law

The framework for the objective analysis of obviousness under 35 U.S.C. 103 is stated in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966). Obviousness is a question of law based on underlying factual inquiries. The factual inquiries are as follows:

- (A) Ascertaining the scope and content of the prior art;
- (B) Ascertaining the differences between the claimed invention and the prior art; and
- (C) Resolving the level of ordinary skill in the pertinent art.

Evidence pertaining to considerations as commercial success, long felt but unsolved needs, failure

of others, etc., must also be considered when present.

The Supreme Court in *KSR International Co. v. Teleflex Inc.*, 550 U.S. ___, ___, 82 USPQ2d 1385, 1396 (2007) requires that the analysis supporting a rejection under 35 U.S.C. 103 be made explicit. Quoting *In re Kahn*, 441 F.3d 977, 988, 78 USPQ2d 1329, 1336 (Fed. Cir. 2006), the KSR decision states: "[R]ejections on obviousness cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *KSR*, 550 U.S. at ___, 82 USPQ2d at 1396.

D. The Examiner has Erroneously Ignored the Recited Structure of the Coupling Agent in Rejecting Claims 1-3, 7 and 10-11.

Claim 1 specifies that the tie-layer is prepared by melt modification of one of one of the two polymer materials used in the first and second layers with a coupling agent and that the coupling agent is selected from the group consisting of "*polyepoxides, polyoxazalines, polycarbodiimides, and polyisocyanates*." This language was in the claim in the prior appeal. It was brought to the attention of the Examiner then, and repeatedly in each response since prosecution was reopened. Applicant's efforts have fallen on deaf ears.

In the present rejection the Examiner has changed the combination slightly from the prior appeal but the cited documents are the same. Their content has not been magically supplemented in the meantime.

Except possibly for the Examiner's contention in the Final Action highlighted above that Boer "appears to meet the requirement of the coupling agent in the presently claimed invention," nowhere in the Final Rejection does the Examiner contend that a coupling agent used

in the in any of the tie-layers described in the cited documents is a polyepoxide, polyoxazaline, polycarbodiimide, or polyisocyanate.

In particular, the Examiner does not assert that Plexar® polymers of Wang are modified with any of these coupling agents. The Examiner further does not assert that Samuelson et al or Shimura et al use such a coupling agent. Instead the Examiner's comments only go to use of *anhydride* or *acid* modified polymers as tie-layers. Claim 1 does not call for the coupling agent to be an anhydride or an acid. The Examiner is simply ignoring the structural recitation for the coupling agent.

As noted above the Final Action states at one point that Boer et al meets the coupling agent recitation. This is clearly wrong.

The Final Action does not explain how "(a) a polyamine and (b) polyamide-forming monomers selected from lactams, aminocarboxylic acid, and/or equimolar combinations of diamine and dicarboxylic acid (see paragraph bridging col. 2-3), and 0.01-4.2 mol of an oligocarboxylic acid (see col. 4, ln. 8-13)" meets the recitation of a polyepoxide, a polyoxazaline, a polycarbodiimide, or a polyisocyanate. It does not.

The Examiner's statement that Boer "appears to meet the requirement of the coupling agent in the presently claimed invention" is a complete fiction. It has no support in the document. This kind of fictional assertion is not a "finding" and has no place in the Examination process.

Boer et al pertains to laminates which use an adhesion promoter layer between two polymer layers which Boer et al designates as layers I and II, respectively. However the Boer et al adhesion promoter layer is not formed using any of the coupling agents identified in claim 1. The adhesion promoters of Boer et al comprise a graft copolymer prepared using the following

monomers:

- a) from 0.5 to 25% by weight, based on the graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol
- b) polyamide-forming monomers selected from lactams, ω -aminocarboxylic acids and/or equimolar combinations of diamine and dicarboxylic acid. [Col. 2, line 55 - col. 3, line 6.]

These components are not polyepoxides, polyoxazalines, polycarbodiimides, or

polyisocyanates, nor are the graft copolymers prepared therefrom.

Boer et al also mentions as other optional ingredients of the adhesion promoter composition:

- II. from 10 to 85 parts by weight of a polyamide;
- III. from 10 to 85 parts by weight of a polyester; where the sum of the parts by weight of I, II and III is 100; and
- IV. a maximum of 40 parts by weight of additives selected from impact-modifying rubber and/or conventional auxiliaries or added materials. [Col. 8, lines 7-25.]

As to items II and III, *these also are not polyepoxides, polyoxazalines, polycarbodiimides, or polyisocyanates*. As to item IV, as examples of impact-modifying rubbers, Boer identifies:

[E]thylene-propylene or ethylene-propylene-diene copolymers (EPA-0 295 076), polypentenylene, polyoctenylene, random or block copolymers of alkenyl-aromatic compounds with aliphatic olefins or dienes (EP-A-0261 748) or core/shell rubbers having a tough, elastic core of (meth)acrylate, butadiene or styrenebutadiene rubber having glass transition temperatures (T_g) of $<-10^\circ\text{C}$, where the core may be crosslinked and the shell may be built up from styrene and/or methyl methacrylate and/or further unsaturated monomers (DE-A 21 44 528 and 37 28 685). [Col. 8, lines 48-53; Col. 6, lines 46-54; col. 7, lines 36-40.]

These also are not polyepoxides, polyoxazalines, polycarbodiimides, or polyisocyanates.

Finally, as to conventional auxiliaries or added materials Boer identifies:

flame retardants, stabilizers, plasticizers, processing auxiliaries, fillers, in particular fillers which improve the electrical conductivity, reinforcing fibers, pigments or the like. [Col. 6, lines 55-62; col. 7, lines 40-47]

Once again, there is no teaching of polyepoxides, polyoxazalines, polycarbodiimides, or

polyisocyanates.

The Examiner has pointed to *nothing* in the Boer et al reference that can be identified as a teaching to employ a polyepoxide, polyoxazoline, polycarbodiimide, or polyisocyanate as the coupling agent in the Boer et al adhesion promoter layer. No such teaching can be found.

In the basic *Graham* obviousness analysis the Examiner has clearly erred both in determining the content of the prior art and in ascertaining the differences between the prior art and the claimed invention. Because of these errors the Examiner has not have a *prima facie* case of obviousness. The rejection of claim 1, and of claims 2-3, 7 and 10-11 which depend therefrom, must be reversed.

E. Conclusion

The Examiner's contentions that claims 1-3, 7 and 10-11, are obvious from Wang et al, US 5,195,969, Samuelson et al, US 6,464,683 or Boer et al, US 6,355,358 in view of Shimura et al, US 5,441,488 has been shown to be clearly wrong. None of the documents uses a tie layer formed with a coupling agent as recited in claim 1. The combinations do not make out a *prima facie* case of obviousness. The Board is respectfully requested to reverse the rejections with instruction to pass the application to issue.

Respectfully submitted,

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(viii) Claims Appendix

A. Claims on Appeal

1. An article comprising a laminate having first and second layers and a tie-layer therebetween bonding the first and second layers, the first and second layers formed, respectively, of first and second polymer materials, the first and second polymer materials being different, wherein

the first and second polymer materials, respectively, have first and second functional groups thereon, and

the tie layer is formed of a tie-layer polymer material obtained by melt modification of one of the first or the second polymer materials, said melt modification comprising incorporation therein of at least 5% by weight of a coupling agent, the coupling agent having functional groups thereon, at least some of which are reactive in the melt with at least the functional groups on the other of said first and second polymer materials, said coupling agent being selected from the group consisting of polyepoxides, polyoxazalines, polycarbodiimides, and polyisocyanates.

2. An article as in claim 1 wherein the coupling agent functional groups further comprise functional groups which are reactive in the melt with the functional groups of said one of the first and second polymer materials.

3. An article as in claim 1 wherein the tie layer polymer has been crosslinked after formation of the laminate.

7. An article as in claim 1 wherein the first polymer material is a polyester or a polyamide, the second polymer material is a polyolefin and the tie layer material is obtained by modifying the second polymer material.

10. An article as in claim 1 wherein the coupling agent is incorporated into the tie layer material in an amount of from about 7% to about 35% by weight.

11. An article as in claim 1 wherein the coupling agent is incorporated into the tie layer material in an amount of 10-20% by weight.

B. Claims Pending but Withdrawn

45. Medical device tubing of a catheter or of a parison for forming a medical balloon comprising a laminate, the laminate comprising three adjacent layers, a first layer a second layer and a tie-layer therebetween, the laminate formed by melt coextrusion using a pair of polymer materials of different polymers to produce the three layers, the first layer being formed of one of said pair of polymer materials, the second layer being formed of the second of the pair of polymer materials, and the tie layer being formed from the second of said pair of polymer materials by a melt modification thereof to produce a tie-layer material, the melt modification comprising incorporation therein of a coupling agent having functional groups thereon which are reactive in the melt with functional groups on the first of said first and second polymer materials.

46. (Withdrawn - Previously Presented) A tubing segment as in claim 45 wherein said melt modification produced a substantial degradation of the molecular weight of the second polymer material used to prepare the tie-layer material.

47. Medical device tubing as in claim 45 wherein said coupling agent is incorporated into the tie layer material in an amount of at least 0.5% by weight.

48. Medical device tubing as in claim 45 wherein the coupling agent is incorporated into the tie layer material in an amount of from about 7% to about 35% by weight.

49. Medical device tubing as in claim 45 wherein the coupling agent is incorporated into the tie layer material in an amount of 10-20% by weight.

50. Medical device tubing as in claim 45 wherein the coupling agent is an anhydride of a polycarboxylic acid.

51. Medical device tubing as in claim 45 the coupling agent is a member of the group

consisting of polyepoxides, polyoxazalines, polycarbodiimides, and polyisocyanates.

52. Medical device tubing as in claim 45 wherein the coupling agent functional groups further comprise functional groups which are reactive in the melt with functional groups of said first polymer material.

53 Medical device tubing as in claim 45 wherein the first layer is an inner layer and the second layer is an outer layer.

54. Medical device tubing as in claim 45 wherein the first layer is an outer layer and the second layer is an inner layer.

55. Medical device tubing as in claim 45 wherein the tie layer polymer has been crosslinked after formation of the laminate.

56. Medical device tubing as in claim 45 wherein at least a portion of the second polymer material and the tie-layer polymer material have been crosslinked after formation of the laminate.

57. Medical device tubing as in claim 45 wherein one of the first and second polymer materials is a polyester and the other of the first and second polymer materials is a polyolefin or a polyamide.

58. Medical device tubing as in claim 45 wherein the tie layer is partially diffused into the second layer.

59. Medical device tubing as in claim 45 the tie layer material further having incorporated therein a catalyst for reaction of the coupling agent with functional groups in the second polymer material.

60. Medical device tubing as in claim 59 wherein the catalyst is selected from the group consisting of tri-valent phosphorous compounds, pentavalent phosphoric compounds, tin

compounds, titanate compounds, tertiary amines, blocked amines, and mixtures thereof.

61. Medical device tubing as in claim 45 wherein the second layer is formed of a polyolefin polymer material.

62. Medical device tubing as in claim 61 wherein said melt modification produced a substantial degradation of the molecular weight of the second polymer material used to prepare the tie-layer material and wherein the tie layer polymer has been irradiatively crosslinked after formation of the laminate.

63. A tubing segment of catheter tubing or of a parison for forming a medical balloon comprising a laminate having first and second layers and a tie-layer therebetween bonding the first and second layers, the first and second layers formed, respectively, of first and second polymers, the first and second polymers being different, wherein

the first and second polymers, respectively, have first and second functional groups thereon, and

the tie layer is formed of a tie-layer polymer material obtained by melt modification of one of the first or the second polymers, said melt modification comprising incorporation therein of at least 5% by weight of a coupling agent, the coupling agent having functional groups thereon, at least some of which are reactive in the melt with at least the functional groups on the other of said first and second polymers, said coupling agent being selected from the group consisting of polyepoxides, polyoxazalines, polycarbodiimides, and polyisocyanates.

(ix) Evidence appendix.

- A. Wang et al, US 5,195,969
- B. Samuelson et al, US 6,464,683
- C. Boer et al US 6,355,358
- D. Shimura et al, US 5,441,488

(x) Related proceedings appendix.

Not applicable



US00519596A

United States Patent [19]

Wang et al.

[11] **Patent Number:** 5,195,969[45] **Date of Patent:** Mar. 23, 1993[54] **CO-EXTRUDED MEDICAL BALLOONS AND CATHETER USING SUCH BALLOONS**[75] **Inventors:** James C. Wang, Norton; George R. Roberts, Arlington; Brian A. Pederson, Sr., So. Attleboro, all of Mass.[73] **Assignee:** Boston Scientific Corporation, Watertown, Mass.[21] **Appl. No.:** 691,999[22] **Filed:** Apr. 26, 1991[51] **Int. Cl.⁵** A61M 29/00[52] **U.S. Cl.** 604/96; 604/103[58] **Field of Search** 604/96, 97, 98, 99, 604/100, 101, 102, 103; 606/191-194[56] **References Cited****U.S. PATENT DOCUMENTS**

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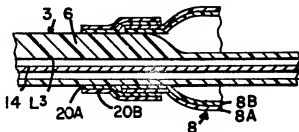
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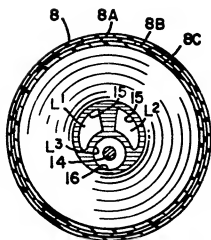
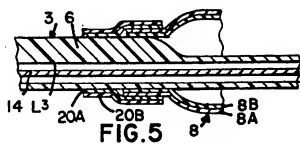
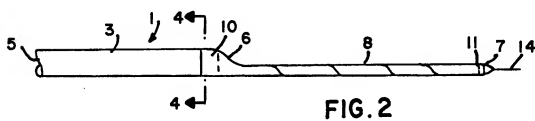
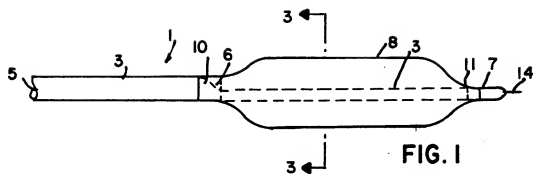
Primary Examiner—John D. Yasko

[57] **ABSTRACT**

A medical balloon and a catheter utilizing the balloon and a mechanism to attach the medical balloon to the catheter tube, and method of making the balloon. The attachment mechanism forms a joint and comprises a plurality of co-extruded and coextensive layers of different polymeric materials, at least one of which is a base structural layer and the other of which is formed of polyethylene and copolymers thereof or of Selar. The base structural layer is thicker than the other layer. The attachment mechanism can be the balloon itself or it can be a sleeve, either of which is heat sealed to the catheter tube. In either case, the diameter of the catheter at the joint is substantially the same as the tube.

16 Claims, 1 Drawing Sheet





CO-EXTRUDED MEDICAL BALLOONS AND CATHETER USING SUCH BALLOONS

BACKGROUND OF THE INVENTION

The present invention relates to balloons for medical devices and medical devices utilizing such balloons. More particularly, the present invention relates to medical or surgical balloons and catheters using such balloons, particularly those designed for angioplasty, valvuloplasty and urological uses and the like. The balloons of the present invention can be tailored to have expansion properties which are desired for a particular use and can be inflated to a predetermined diameter and still be resistant to the formation of pin holes and leakage.

DESCRIPTION OF THE PRIOR ART

In the past, polyethylene, polyethylene terephthalate and polyamide balloons have been used with medical catheters. Polyethylene balloons are particularly advantageous because they can be heat bonded to a like-material substrate and have a relatively low tip diameter, that is the profile of the tip at the connecting joint between the balloon and the catheter can be fairly small. Also, the polyethylene balloons are soft so that they can pass through blood vessels without trauma. Moreover, polyethylene balloons are resistant to the propagation of pin holes, primarily because the walls are thick. But since they are thick, they are large and pass by tight lesions only with great difficulty.

Balloons of polyethylene terephthalate provide low deflated profiles and can have thin walls because such materials have high tensile strengths and adequate burst strength. On the other hand, polyethylene terephthalate balloons require adhesives to bond them to the catheters and adhesive bonding frequently is not dependable and it thickens the catheter at the point of the bond. Moreover, polyethylene terephthalate can have poor pin hole resistance largely due to the very thin walls.

SUMMARY OF THE INVENTION

According to the present invention, it has been discovered that the drawbacks of the polyethylene and the polyethylene terephthalate balloons of the prior art can be remedied through the use of laminated balloon constructions which comprise a tubular body formed of a plurality of co-extruded and co-extensive layers of different polymeric materials.

According to one aspect of the invention, the multilayered balloon combines the advantages of both materials in a balloon, but does not have the disadvantages of either. The balloon includes a layer of a relatively thick, biaxially oriented ethylenic polymeric material such as polyesters, polycarbonates, polyethylene terephthalate and their copolymers, or polyamides such as Nylon. These materials constitute a base structural layer (or layers) and give the balloon its tensile strength and provide for "wear" resistance. The base structural layer may have a thickness between about 0.2 and 1.0 mil. or higher. A second layer is co-extruded with the base structural layer and is co-extensive therewith. The second layer preferably is a polyolefin such as polyethylene and copolymers thereof and can be heat-bonded to a catheter, that is adhesives need not be used. The heat bondable second layer can be disposed on one and preferably both sides of the base structural layer.

In accordance with another aspect of the present invention, the base structural layer again is a material that does not itself readily thermally bond to a polyethylene catheter tubing. In those cases, sleeves of mutually bondable materials are slipped over the joints between the catheter and the balloon and the sleeves are heated to join the balloon to the sleeve and simultaneously join the sleeve to the catheter whereby to act as a fluid-tight seal between the catheter and the balloon.

With regard to multilayered balloons, the second layer (or layers) which is disposed on the base structural layer and co-extruded therewith can also serve as a barrier between the base structural layer and the environment. For example, when a polyamide such as Nylon is used as the base structural layer, a thin layer of maleic anhydride-modified ethylenic polymers such as Plexar can also be co-extruded with it. When layers are disposed on both sides of the base structural layer they keep moisture from effecting the Nylon's properties. Additional layers sometimes may also be co-extruded to bind and the dissimilar layers together in the co-extrusion operation. When Nylon is used, for example, no tying layers are necessary between it and the heat bondable layer. In other cases, however, as when polyester or polycarbonate polymers are used as the base structural layer, adhesion enhancement may be necessary. Such adhesive enhancement may take the form of ultraviolet light irradiation of the product or the incorporation of a co-extruded tying adhesive layer.

With regard to the use of a multilayered sleeve to join the balloon to the catheter, any conventional medical balloon material can be used that does not bond to the catheter without adhesives. The multilayered sleeve can be formed of a base layer of the same material as the balloon with a polyethylene layer disposed on at least the inner side of the sleeve. The polyethylene will adhere to both the catheter and the balloon and form a joint with heat treatment alone.

According to the present invention, the balloons have advantages of both the polyethylene and the materials of the base structural layer. When polyethylene terephthalate is the base, very thin walls can be used with high burst strength. For example, when a typical 3.0 mm. diameter maleic anhydride modified ethylenic polymer layer is co-extruded with a Nylon base structural layer, the resulting balloon can have a wall thickness of 0.5 mil. and a low deflated profile which is comparable with polyethylene terephthalate balloons and is much lower than polyethylene balloons. When using Nylon, the material that is used is biaxially orientable and has higher tensile strength than polyethylene material, thereby resulting in a much thinner wall for comparative burst strength.

It has been found that pin hole resistance of the construction of the present invention is comparable to polyethylene and substantially superior to polyethylene terephthalate. A balloon co-extruded with Sellar has superior abrasion resistance and pin hole resistance than polyethylene terephthalate balloons. Polyamide material is superior to polyethylene terephthalate and polyethylene materials in pin hole resistance. The balloon itself is soft for non-traumatic passage through blood vessels and is comparable to polyethylene because polyamide is not as stiff as polyethylene terephthalate.

In a specific embodiment of a multilayered extruded balloon, it has been found that the use of the above mentioned Sellar PT resin, a trademarked compound (preferably available as Sellar PT 4368 from E. I. Du-

pont de Nemaurs Co. of Wilmington, Del.) as a layer disposed on the base structural layer (or blended with polyethylene terephthalate) will make the balloon more resistant to abrasion and provide it with a softer feel. Sellar coextrusion in multi-layered balloons diminishes pin hole formation and will minimize failure when working with calcified lesions. Moreover, the Sellar may be used as the inner layer of the balloon for use with procedures which include internal electrodes or radiopaque markers which could puncture it.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevational view of a catheter with a multi-layered balloon. The balloon is shown in the distended condition;

FIG. 2 is a view of the same catheter in the folded condition;

FIG. 3 is a cross-sectional view of the balloon of the present invention taken along the line 3—3 of FIG. 1 showing the polymeric layers in the balloon;

FIG. 4 is a cross-sectional view taken along the line 4—4 of FIG. 2 showing the balloon in its folded condition; and

FIG. 5 is a cross sectional view of a distended balloon disposed at the end of a catheter and joined to the catheter by a sleeve.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

An illustrative catheter 1 is shown in FIGS. 1 and 2. Catheter 1 includes a catheter tube 3 having a proximal end 5 a distal end 6 and a tip 7. A distended coextruded medical balloon 8 of the present invention is shown in FIG. 1 secured to the outside of the distal end 6 and the tip 7, the co-extrusion being critical to the present invention. The interior of the balloon 8 is in communication with at least one lumen (not shown in this Figure) of the catheter tube 3. To form the tip 7 (and the portion of the catheter between the distal end 6 and the tip 7 to support the balloon 8) a portion of the catheter tube 3 is cut away so that only the lumen that houses an internal guide wire 14 remains (as shown in dotted lines within the balloon 8).

Extending through the interior of the tube 3 are a plurality of lumens (shown in FIGS. 3 and 4) which can serve a variety of functions, for example, housing the guide wire 14, inserting materials into the blood stream or inflating or deflating the balloon. Except for the balloon 8, all of the various components perform functions which are generally appreciated and known in the art.

To use, the catheter 1 (as shown in FIG. 2) is inserted into the cardiovascular system until the coextruded balloon 8 is located at the site of an occlusion. At this stage, the balloon 8 is typically folded and collapsed and has an external diameter less than the inflated diameter, as can be seen by a comparison of FIGS. 1 and 2. Once the balloon 8 is maneuvered to the location of the occlusion, a pressurizing fluid is inserted at the proximal end 5 of the catheter tube 3 for inflation of the balloon 8. The fluid unfolds the balloon 8 until it presents a relatively smooth expanded profile for imparting forces that are radially outwardly directed at the desired site within the body in order to achieve the desired result of lesion dilation, restriction reduction or similar treatment.

Inserting the catheter 1 in an artery requires that the tube 3 be of a semi-flexible material. Tube 3 preferably is composed of a polyolefin copolymer, for example a

conventional high density polyethylene. The diameter of the tubing is between about 12 and 16 French and may be coated on the inside and outside surfaces with, for example, a silicone based material to promote slippage in an aqueous environment.

As seen in FIGS. 3 and 4, the co-extruded balloon 8 results in a laminated construction. The laminates of the construction include a main structural layer 8B which is generally between about 0.2 and 2.5 mil. or thicker, and formed of one or more biaxially oriented polymers such as polyamides, polyesters, polycarbonates and their copolymers. Co-extruded with and bonded to the structural layer 8B is an inner layer 8C of heat bondable polyolefin such as Plexar. Plexar is an anhydrid-modified polyethylene and a trademarked product sold by Quantum Chemical Corporation of Cincinnati, Ohio. The heat bondable layer 8C is attached directly to the distal end 6 of catheter tube 3 and is secured to the balloon 8 by a heat seal joint 11. A similar joint 11 is formed between the balloon 8 and the catheter tip 7.

The heat bondable layer 8C is co-extruded with the structural layer 8B and has a thickness of between about 0.5 and 1.0 mil. Preferably, two heat bondable layers are co-extruded with the structural layer 8B. The inner layer 8B serves as a mechanism to provide a heat seal joint 10 between the distal end 6 of the catheter tube 3 and the structural layer 8B of the balloon 8. When two layers are co-extruded with the structural layer 8B, the inner layer 8C forms the heat bondable layer and the outer layer 8A forms a protective sheath for the main structural layer 8B. When polyamides such as Nylon are used as the structural layer 8B, Plexar can be used as the heat bonding layer 8C. The outer layer 8A can be formed of the same material and provide for softness for non-traumatic passing through vessels and good pin hole resistance.

An alternative to the construction shown in FIG. 1, another construction is to dispose a balloon formed of a base structural layer 8B of polyethylene terephthalate and an outer layer 8A of polyethylene around the distal end 6 of the catheter tube 3 and then place a sleeve 20 formed of heat bonding layer 20C of high density polyethylene on a base layer 20B Nylon over the end of the balloon 8 whereby the polyethylene of the balloon seals to the polyethylene of the sleeve and the Nylon seals to the catheter 3. In cases where additional strength is needed, an innermost layer can be formed of high density polyethylene and an outermost layer is formed of Nylon with Plexar sandwiched therebetween.

It has been found that where strength, abrasion resistance and/or "feel" are important in medical balloons, that a co-extrusion which includes Sellar resin can be used to provide for these characteristics. The Sellar can be used by itself as the inner and/or outer layer or it can be blended with polyethylene terephthalate. Tests of a 1.6 mil. thick balloon with a Sellar outer layer (a 50/50 blend of Sellar and polyethylene terephthalate) were conducted by rubbing a balloon inflated to 6 atm. and rubbing it back and forth over medium grade emery cloth until failure. The balloons with Sellar or 50/50 blend layers exceeded 200 cycles while a 1.8 mil. thick polyethylene terephthalate balloon failed in 87 cycles. Sellar is a toughened grade of polyethylene terephthalate and it can be co-extruded with the base structural layers herein disclosed according to known techniques.

Referring to FIGS. 3 and 4, the interior of the co-extruded balloon 8 is shown in cross section. In FIG. 3, the balloon is shown in its distended or inflated condi-

tion whereas in FIG. 4 the balloon is shown in its deflated or folded condition. The balloon 8 can typically have an outer diameter that can be on the order of roughly three to six and even more times the outer diameter of the catheter tube 3. Pressurized fluids are used to inflate the balloon include and those conventionally used in the art, such as the well known aqueous solutions can be used if they do not pose a problem of leaving residual fluids or chemically reacting with the balloon. Such fluids are introduced into the balloon 8 and removed therefrom through a lumen L¹ which is in fluid flow relationship with the interior thereof. Venting of gasses initially trapped in the catheter and the balloon prior to introduction of the inflation fluids is accomplished by expelling them through a second lumen L² also formed in the interior of the catheter tube 3. Preferably, lumen L¹ and L² are cut off at joint 10 so as to leave only a third lumen L³.

The third lumen L³ houses a guide wire 14 that passes through the balloon 8 and the tip 7. The third lumen L³ is different than the other two lumens, L¹ and L², in that it extends entirely through the balloon 8 from the distal end 6 to the tip 7 so as to sheath the guide wire. In some embodiments, it may be desirable to combine the functions of lumens, L¹ and L², to only have a single lumen for inflating or deflating the balloon. Lastly, the lumen defined by L³ provides for a housing for a guide wire 14 which may be removably housed in it. Guide wire 14 passes through the entire length of the catheter 3 and through the balloon 8 (while preferably sheathed in lumen L³ and thence into a axial bore (not shown) in tip 7 to emerge from the end of tip 7 (as shown in FIGS. 2 and 3).

Each of the lumens L¹, L² and L³ is formed by walls 15 and 16 that are extruded as the catheter tube is extruded from an extrusion machine, as is well known in the art. The thickness of the walls 15 and 16 can be between 0.5 and 10 mil. as is well known.

As shown in FIG. 4, the diameter of the folded balloon 8 is substantially the same or less than the diameter of the catheter tube 3 so as to provide for easy passage of the catheter through blood vessels. The extruded tubing 3 has a nominal wall thickness that generally is on the order of six to twelve times the desired wall thickness of the balloon 8.

To form the co-extruded balloons, the materials initially are melted separately in extrusion machines. When melted, the materials are separately forced into an extrusion head and extruded so that they are forced out as a plurality of layers in the form of a single tube which critically forms the balloon of the present invention. A Nylon-Plexar or polyethylene-polyethylene terephthalate balloon may be formed by taking a six inch length of the three layered tubing which is to be manufactured into a balloon and in a holding fixture. The left hand end of the tube is attached to a Touby Borst adapter. The right hand end of the tube is heat sealed to temporarily prevent pressurized air from escaping. The right hand end is attached to a tension line which is pulled for the force of a least 150 grams (for a 3.0 mm. diameter balloon). The tubing is heated under a pressure of between about 100 and 400 psi to about 210° F. for several seconds. Afterwards, the heated area is cooled and the support frame is spread apart slightly so as to expose a predetermined section of tubing to permit the balloon area to be reheated to a temperature between about 210° and 220° F. to permit the balloon to be expanded to a desired diameter under pressure for about

35 seconds. The pressure is then stopped and the deflators are slid to the ends of the balloon and the balloon is heated for a third time to about 310° F. to heat set the balloon and biaxially orient the polymeric matrix. This third heating prevents the balloon layers from flaking and prevents the balloon from expanding beyond the size at which it will set during the heat setting period. The heat setting takes about 8 seconds.

For a Nylon-Plexar balloon, the deflators from the tubes are then removed and another unheated tube is mounted into the fixture. The catheter tube is slid inside the balloon so that it engages the heat bondable polyethylene layer. The balloon is bonded to the polyethylene shaft by heat bonding in a temperature of about 310° F. which is long enough the melt the polyethylene end and the inner layer of the polyethylene together.

It is quite important to recognize that the heat treatment steps as described herein essentially prevent the delamination of the heat bondable layers 8C and 8A from the main structural layer 8B as is required when a laminated construction is used as a catheter. Flaking and delamination is not a problem however, with polyethylene terephthalate and Sellar layers.

While it is apparent that modifications and changes may be made within the spirit and scope of the present invention. It is intended, however, only to be limited by the scope of the appended claims.

We claim:

1. A catheter for medical purposes, said catheter comprising:

a tubular member having a distal end and at least one lumen disposed therethrough;

a balloon having at least one open end, said open end being sealed at a joint to said distal end, the interior of said balloon being in communication with said lumen, said balloon having an elongated tubular body and comprising a plurality of co-extruded layers of different polymeric materials, at least one of said layers being a polyolefin that is sealed by heat to said tubular member.

2. The catheter according to claim 1 wherein the other of said layers is formed of a material comprising polyethylene and copolymers thereof.

3. The catheter according to claim 1 wherein the diameter of the tubular member and the diameter of said joint is substantially the same.

4. The catheter according to claim 1 wherein another of said layers is a base structural layer and has a thickness between about 0.2 and about 2.5 mil. and the other layer has a thickness between about 0.15 and 1.0 mil.

5. The catheter according to claim 1 wherein said balloon has at least three co-extruded layers, one of said layers being a base structural layer, said base structural layer being disposed between the two layers at least one of which is the heat sealed layer.

6. The catheter according to claim 1 wherein said balloon has a base structural layer, said base structural layer being a member selected from the group consisting of polyamides, polycarbonates, polyesters and copolymers thereof.

7. The catheter according to claim 1 wherein the heat sealable layer of said balloon is a member selected from the group consisting of polyethylene and copolymers thereof.

8. The catheter according to claim 1 wherein the tubular member is formed of a polyolefin comprising polyethylene and said polyolefin is a member selected from the group consisting of polyamides, polycarbon-

ates, polyesters and copolymers thereof and said heat sealable layer is a member selected from the group consisting of polyethylene and copolymers thereof.

9. The catheter according to claim 1 wherein said balloon has two open ends, said catheter further comprising a distal tip, said distal tip being heat sealed to said balloon.

10. A catheter for medical purposes, said catheter comprising:

a tubular member having a distal end and at least one lumen disposed therethrough;

a balloon having at least one open end, said open end being sealed at a joint to said distal end, the interior of said balloon being in communication with said lumen, said balloon having an elongated tubular body and comprising a plurality of co-extruded layers of different polymeric materials, at least one of said layers being a base structural layer and the other of said layers being formed of a Selar.

11. A catheter for medical purposes, said catheter comprising:

a tubular member having a distal end and at least one lumen disposed therein;

an elongated medical balloon having an open end, said open end being fitted over a joint at said distal end of said tubular member, the interior of said balloon being in communication with said lumen, said balloon having an elongated, expandable tubular body and comprising a plurality of co-extruded

layers of different polymeric materials, neither of which is heat sealed to said tubular member;

a sleeve for connecting said medical balloon to said tubular member, said sleeve being disposed over said joint and comprising an elongated tubular body having a predetermined diameter and adhering to both said medical balloon and said catheter, said sleeve comprising a plurality of co-extruded and coextensive layers of different polymeric materials, at least one of said layers being a polymeric layer and another of said layers being selected from the group consisting of polyethylene and copolymers thereof.

12. The catheter according to claim 11 wherein said tubular member is formed of a material comprising polyethylene and copolymers thereof.

13. The catheter according to claim 11 wherein the diameter of the tubular member and the diameter of the joint is substantially the same.

14. The catheter according to claim 11 wherein the balloon has a layer selected from the group consisting of polyamides, polycarbonates, polyesters and copolymers thereof.

15. The catheter according to claim 11 wherein the sleeve has a layer selected from the group consisting of polyamides, polycarbonates, polyesters and copolymers thereof.

16. The catheter according to claim 11 wherein said balloon has two open ends, said catheter further comprising a tip disposed on the other open end, said tip being heat sealed to said balloon.

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(12) **United States Patent**
Samuelson et al.

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(45) Date of Patent: ***Oct. 15, 2002**

- (54) **TRILAYER, EXTRUDED MEDICAL TUBING AND MEDICAL DEVICES INCORPORATING SUCH TUBBING**
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- (*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 50 days.

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Related U.S. Application Data

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- (51) Int. Cl.⁷ **A61M 25/00; A61M 29/00**
(52) U.S. Cl. **604/524; 604/96.01**
(58) Field of Search **604/96.01, 264, 604/524-527**

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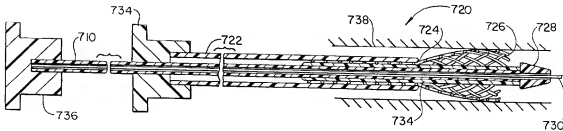
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- (57) **ABSTRACT**

The present invention provides a length of trilayer, extruded, medical tubing comprising an outer layer, a core layer, and an intermediate tie layer. The outer layer comprises a polymer that is directly bondable, while the core layer comprises a lubricious polymer. The core layer thus defines a lumen that exhibits the desired characteristics, i.e., low friction for the advancement of a guidewire or catheter through the lumen without comprising the strength and stiffness that is desirable in tubing that is to be used in medical devices. Additionally, the tubing is easily coextruded and yet, is not subject to delamination, thus providing the added advantage of providing a reduction in the overall cost of manufacture.

23 Claims, 3 Drawing Sheets



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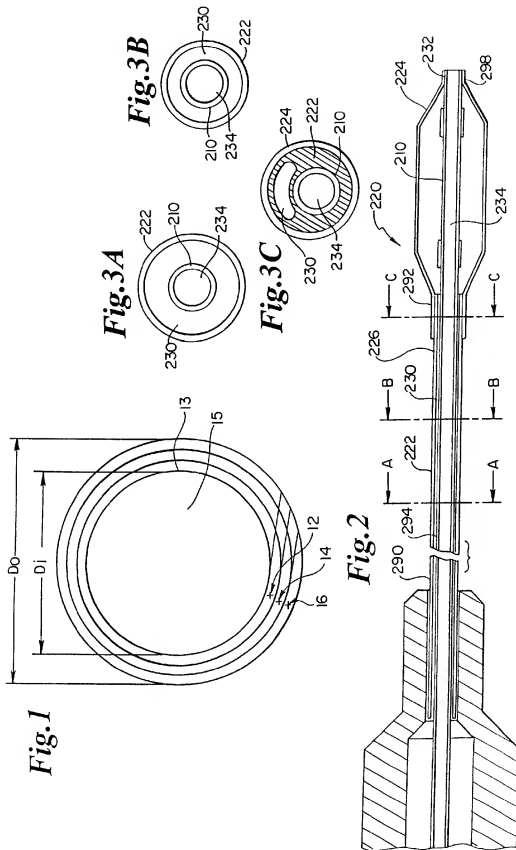


Fig. 4

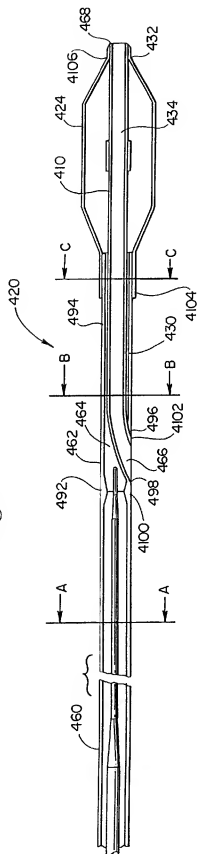


Fig. 5C

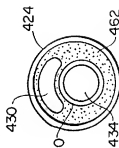


Fig. 5B

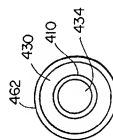


Fig. 5A

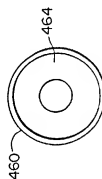
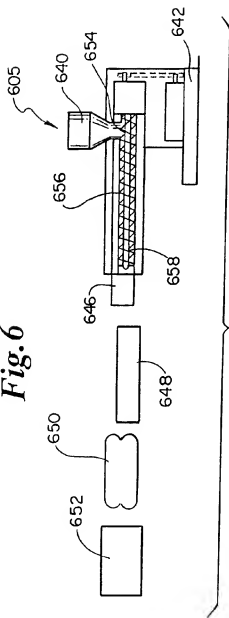
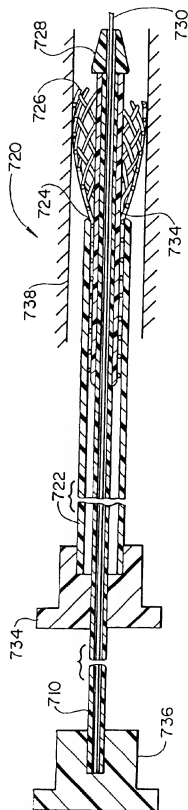


Fig. 6*Fig. 7*

TRILAYER, EXTRUDED MEDICAL TUBING AND MEDICAL DEVICES INCORPORATING SUCH TUBING

This application is a continuation 09/014,789 filed Jan. 28, 1998 of U.S. Pat. No. 6,165,166, which claims priority to Provisional Application Ser. No. 60/044,879, filed Apr. 25, 1977.

FIELD OF THE INVENTION

The present invention pertains generally to medical tubing and medical devices incorporating such tubing. More specifically, the present invention pertains to medical tubing and corresponding medical devices adapted for percutaneous transluminal use, such as guide catheters, diagnostic catheters such as illustrated in U.S. Pat. No. 5,403,292, and balloon catheters such as illustrated in U.S. Pat. No. 4,762,129. Medical tubing of the present invention is particularly useful to structurally define the lumen of a catheter, e.g., a rapid-exchange balloon catheter or an over-the-wire catheter. The tubing of the present invention is also useful as an inner member in a stent delivery device.

BACKGROUND OF THE INVENTION

Intravascular catheters are presently in wide clinical use for a variety of diagnostic and therapeutic purposes. Intravascular catheterization therapies, such as angioplasty, atherectomy, and laser irradiation, have been developed as alternatives to bypass surgery for treating vascular diseases or other conditions that occlude or reduce the lumen size of portions of a patient's vascular system. In particular, balloon angioplasty has proven to be a useful, and in many circumstances, a preferred treatment for obstructive coronary diseases. Also, intravascular diagnostic catheters for angiographies, ultrasonic imaging, and Doppler blood flow measurements for example, have been developed to measure or image the extent of the occlusion of a vessel, (e.g., stenosis). These intravascular diagnostic catheters may be used in conjunction with the aforementioned therapeutic catheters or may be used in conjunction with more invasive techniques such as coronary surgery. Intravascular therapeutic and diagnostic catheters have achieved acceptance because of their effectiveness as well as the fact that their use typically involves a relatively minor surgical procedure as compared to coronary bypass surgery.

However, the effectiveness of the techniques employing these catheters may at times be dependent upon the positioning of the catheter into the vascular system of a patient via an incision at an accessible location which may be remote from the site of occlusion or stenosis. Typically, for example, the intravascular catheter may be introduced into the femoral artery through an incision at the groin and then advanced through the femoral artery to the desired distal coronary site. Because of the small size of some of these vessels and the tortuous passages through the vessels, positioning of a catheter through a patient's vasculature can be a difficult and time consuming task. Furthermore, the catheters must be able to traverse these tortuous pathways in a manner as atraumatic to the patient as possible. Therefore, in order to limit insertion time and discomfort to the patient, intravascular catheters will preferably have several performance characteristics.

First of all, an intravascular catheter should exhibit good torque control such that manipulation of a proximal portion of the catheter is responsively translated to the tip or distal portion of the catheter. Moreover, the catheter should have

sufficient strength in the longitudinal direction so as not to kink or fold as it is advanced through the vascular system. Also, for some types of intravascular catheters, it is desirable to maximize the inner diameter relative to the outer diameter, i.e., to make the lumen as large as practically possible. Specifically, for example, diagnostic catheters generally possess a relatively large lumen to allow fluids, such as radiopaque contrast fluid, to be injected therethrough and out the distal end so that the area of the vascular system under investigation can be viewed fluoroscopically.

Additionally, if the catheter is a dilation catheter, the outer surface of the tubing to be used in an intravascular catheter must be bondable to balloon material. Although the tubing may be bonded to the balloon with adhesive, this is not optimal as the adhesive may fail. Additionally, the adhesive undesirably adds to the surface profile of the catheter. Thus, it is preferable that the outer surface of the tubing of the catheter be directly bondable to the balloon material, such as by fusion bonding, described in U.S. Pat. Nos. 5,501,759 and 5,267,959.

Finally, catheter balloons are now being inflated to higher pressures than has been previously conventional in the art. For example, until recently, balloon inflation pressures typically averaged approximately 12 atmospheres. However, one current trend involves inflating balloons to pressures as high as 28 atmospheres. This relatively high pressure tends to stretch and constrict tubing if the tubing is too weak. In severe cases, the tubing could rupture. Thus, in order to be useful in a balloon catheter involving higher pressures, the tubing must be strong enough to withstand this higher pressure without collapsing or rupturing.

The internal lumen surface of intravascular catheters is subject to performance demands as well. For example, an important function of the internal lumen surface of intravascular catheters is to provide very low surface friction between the catheter and a guidewire and/or treatment device slidably engaging the lumen surface. The low friction internal surface facilitates advancement of the catheter over the guidewire or the advancement of the treatment device through the catheter lumen, as the case may be. Lubricity is especially critical in the curved portion of guide catheters. The low friction internal surface has typically been provided by the use of a lubricious polymer, e.g., polytetrafluoroethylene or the like, as the internal surface material, or alternatively, by coating the internal lumen surface of the catheter with a friction reducing material, such as liquid silicone.

In sum, catheter tubing should possess a combination of the desired characteristics of strength, pushability, torqueability, bondability and lubricity. However, such a combination of characteristics has not been achieved satisfactorily with tubing comprising only a single material. First of all, medical tubing formed from an inherently lubricious polymer tends to be difficult to effectively bond to the material of conventional balloons due to the chemical incompatibility between the materials to be bonded. On the other hand, polymer materials that demonstrate good bonding characteristics with balloons typically must be coated with a lubricant on the interior surface so that the interior surface is sufficiently lubricious, necessitating an additional manufacturing step. Furthermore, such lubricants tend to wear off, so that lubricity is diminished over time.

The prior art also describes several attempts to provide the desired characteristics by utilizing multilayered tubing in intravascular catheters. Conventionally, such multilayered tubing comprises an outer layer of a bondable material such

as nylon, polyethylene, polyurethane, or poly(ethylene terephthalate) and an inner layer of a lubricious material such as polytetrafluoroethylene (PTFE) or other lubricious polymer, e.g., high density polyethylene. For example, U.S. Pat. No. 5,538,510 describes a coextrudable, flexible tubing which comprises an outer layer and an inner layer, the two layers being different materials and being covalently bonded to each other. Specifically, the patent purports to provide a length of tubing with the desired combination of properties by using a lubricious polymer as the inner layer, and a stiff polymer as the outer layer. The patent discloses that the flexible tubing is coextrudable and, furthermore, that the lumen of the tubing is sufficiently lubricious so as to obviate the use of a separate low friction sleeve and/or coating. Additionally, U.S. Pat. No. 4,707,389 describes a multi-layered tube composed of an outer layer of ethylenevinylacetate (EVA) and an inner layer of polyvinylchloride (PVC), bonded together by a bonding layer. Finally, U.S. Pat. No. 3,561,493 discloses a multi-layered tubing in which the inner and outer layers are welded together by a precompounded layer of the two different polymers.

Although each of these patents purport to provide tubing and/or medical devices with the desired characteristics, problems still remain with existing multilayer tubing structures. For example, the low friction polymeric materials capable of providing a sufficiently lubricious lumen are generally chemically incompatible with the polymeric materials that are capable of providing adequate performance as the catheter outer layer. As a result of this chemical incompatibility, these different classes of materials do not form significant bonds with each other, even upon coextrusion, and thus, tubing comprising layers of these dissimilar materials tends to be subject to delamination. Further, substantial differences between the mechanical properties of the two classes of polymer materials further exacerbates this incompatibility problem.

There is thus a need in the art for medical tubing and medical devices incorporating such tubing that exhibit the desired characteristics of strength, pushability, torqueability, bondability and lumen lubricity. These and other objects are accomplished by the present invention, as hereinafter described.

SUMMARY OF THE INVENTION

According to the present invention, the above objectives and other objectives apparent to those skilled in the art upon reading this disclosure are attained by the present invention which is drawn to trilayered tubing as well as to a medical device suitable for percutaneous transluminal use comprising the tubing. More specifically, it is an object of the present invention to provide coextruded, flexible, trilayered tubing, wherein the three layers are firmly bonded together such that the layers resist delamination under operating conditions both normal and extreme (e.g., high balloon pressures of up to 28 atmospheres or more) and furthermore, wherein the materials that comprise the three layers provide the tubing with the desirable characteristics for tubing that is to be used in a medical device suitable for percutaneous transluminal use.

Generally, the present invention provides a length of coextruded, flexible tubing that meets the needs and objectives described hereinabove, by virtue of a multilayer structure. Specifically, the multilayer structure comprises a core layer of a lubricious polymeric material, an outer layer comprising directly bondable (defined below) polymer, and an intermediate tie layer comprising a polymer having

pendant functionality capable of adhering the lubricious material of the core layer to the directly bondable material of the outer layer. In this manner, the intermediate tie layer provides a strong connection between the core layer and the outer layer.

In preferred embodiments, the glass transition temperature (T_g) characteristics of the intermediate tie layer are selected to be in between those of the core layer and the outer layer. Specifically, it is preferred that the glass transition temperatures vary only gradually from the core layer to the outer layer in order to provide a stage-wise transition of mechanical characteristics from the material of the outer layer to the material of the core layer. Preferably, the glass transition temperature of each layer will be from 85% to 115% of the glass transition temperature of the material(s) adjacent to it. By providing a gradient in the T_g from the core layer to the outer layer, a more stable, more compatible, trilayered tubing is provided that possesses the desired characteristics of strength, pushability, torqueability, bondability, and a lubricious lumen, while also demonstrating dramatically improved resistance against delamination.

The present invention thus provides a length of coextruded, flexible tubing comprising an outer layer having a first glass transition temperature, an intermediate tie layer having a second glass transition temperature, and a core layer having a third glass transition temperature. Preferably, the first glass transition temperature is greater than the second glass transition temperature, which is preferably greater than the third glass transition temperature. Additionally, it is preferred that the outer layer be comprised of a material that is directly bondable to conventional balloon materials. It is further preferred that the core layer is comprised of a material that is lubricious and that the intermediate tie layer is comprised of a material that comprises functionality capable of adhering to both the material of the outer layer and the material of the core layer.

In another aspect, there is also provided a medical device suitable for percutaneous transluminal use comprising the tubing of the present invention and a radially expansive component operationally coupled to the tubing. For example, the tubing of the present invention may be utilized to define the guidewire lumen of a balloon catheter. More specifically, the trilayer tubing of the present invention may define the guidewire lumen of an over-the-wire catheter, i.e., where the guidewire lumen is defined by the trilayered tubing runs the entire length of the catheter. The tubing of the present invention may also define the guidewire lumen of a rapid exchange catheter, i.e., wherein one end of the guidewire lumen is defined by the tubing of the present invention extends through the distal end of the catheter and the opposite end exits through an outer wall of the catheter. Additionally, the trilayered tubing of the present invention may be utilized to form the inner member of a stent-delivery device, wherein a stent is releasably mounted to the tubing of the present invention.

As used herein, the phrase "direct bond" (or "directly bondable") is meant to indicate a bond between two materials that requires no bonding substance, i.e., adhesive, interposed between the materials (or materials that are so bondable). Additionally, the term "lubricious" as applied to the materials herein is meant to indicate a material that has a kinetic coefficient of friction (steel on polymer) of less than about 0.5. As used herein, "elastomeric" is meant to indicate that property of a material that allows the material to be stretched to at least twice their original length and to recover its original shape partially or completely after the deforming force has been removed. "Glass transition temperature" or

"T_g" as used herein and as is generally known to those of skill in the art, refers to that temperature at which an amorphous material changes from a brittle vitreous state to a plastic state and may be determined by Differential Scanning Calorimetry (DSC). Finally, as used herein, the phrase "acid-functional" is meant to indicate materials that have pendant acidic functional groups.

BRIEF DESCRIPTION OF THE DRAWINGS

The above mentioned and other advantages of the present invention, and the manner of attaining them, will become apparent and the invention itself will be better understood by reference to the following description of the embodiments of the invention taken in conjunction with the accompanying drawings, wherein:

FIG. 1 is an enlarged, cross-sectional view of one embodiment of tubing in accordance with the present invention;

FIG. 2 is a longitudinal sectional view of an over-the-wire angioplasty catheter in accordance with the present invention;

FIG. 3A is an enlarged, cross-sectional view taken along line A—A of FIG. 2;

FIG. 3B is an enlarged, cross-sectional view taken along line B—B of FIG. 2;

FIG. 3C is an enlarged, cross-sectional view taken along line C—C of FIG. 2;

FIG. 4 is a longitudinal sectional view of a rapid exchange angioplasty catheter in accordance with the present invention;

FIG. 5A is an enlarged, cross-sectional view taken along line A—A of FIG. 4;

FIG. 5B is an enlarged, cross-sectional view taken along line B—B of FIG. 4;

FIG. 5C is an enlarged, cross-sectional view taken along line C—C of FIG. 4;

FIG. 6 is a schematic view of an extrusion system capable of extruding the tubing of the present invention; and

FIG. 7 is a longitudinal sectional view of a stent delivery device in accordance with the present invention

DETAILED DESCRIPTION OF THE INVENTION

The embodiments of the present invention described below are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the following detailed description. Rather the embodiments are chosen and described so that others skilled in the art may appreciate and understand the principles and practices of the present invention.

According to the present invention, trilayer tubing 10 is illustrated in cross-sectional view in FIG. 1. In accordance with the present invention, tubing 10 comprises outer layer 16, intermediate tie layer 14, and core layer 12, the polymeric materials of the outer, tie and core layers typically being different and being formed preferably by coextruding. Inner surface 13 of trilayer tubing 10 defines lumen 15.

Outer layer 16 is preferably comprised of at least one directly bondable polymer. That is, outer layer 16 is preferably comprises of at least one polymer selected so as to be directly bondable to the balloon by a technique such as fusion bonding. A wide variety of polymers may be incorporated into outer layer 16. Preferably, the material chosen for use in outer layer 16 will be thermoplastic, so as to be more easily extrudable. It is further preferred that the

material chosen for use in outer layer 16 will be elastomeric. Generally, preferred polymers for use in outer layer 16 have a weight average molecular weight in the range of from about 40,000 to about 100,000.

Outer layer 16 may preferably comprise a polyester, a polyamide or combinations thereof. Exemplary polyesters which are suitable for use in outer layer 16 include polyesters containing both polyether and polyester segments. Particularly suitable are the family of polyether polyesters commercially available under the trade name Hytel® from E.I. DuPont De Nemours and Company, Wilmington, Del. Also well-suited for use in outer layer 16 of tubing 10 of the present invention are the family of polyesters available under the trade name Arnite® from DSM Engineering Plastics, Evansville, Ind.

Polyamides suitable for use in outer layer 16 in tubing 10 of the present invention include Nylon 12, Nylon 6/6 or other nylon copolymers, as well as polyether block amides. An example of a commercially available polyamide suitable for use in outer layer 16 in the tubing 10 of the present invention is available under the trade name PEBAX® from Atochem Inc., Glen Rock, N.J.

Core layer 12 is preferably made of at least one lubricious polymeric material to facilitate the advancement over a guidewire or advancement of a separate, smaller catheter through lumen 15 of tubing 10. Although it is preferred that core layer 12 be sufficiently lubricious without such a coating, a solid or liquid lubricant may coat the surface of lumen 15 as structurally defined by core layer 12, and thus such a coating is understood to be within the scope of the present invention. As discussed hereinabove, lubricious materials, as used herein, preferably are those materials with a kinetic coefficient of friction (steel on polymer) of less than about 0.5. Generally, preferred lubricious polymers have a weight average molecular weight in the range of from about 80,000 to about 300,000.

As representative examples, the at least one lubricious polymeric material incorporated into core layer 12 may preferably be selected from an olefinic polymer, a fluorinated polymer, or combinations thereof. More preferably, the material of core layer 12, if an olefinic polymer, may comprise a high density polyethylene, an ultra high density polyethylene, a low density polyethylene, a linear low density polyethylene, or combinations thereof. Such polyethylene resins are commercially available from the Quantum Chemical Company, Cincinnati, Ohio, under the trade name Petrothene® LS 5060-00 and LM 6007-00. Additional materials that are believed to be suitable in core layer 12 include fluorinated polymers such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). Because PVDF is much easier and practical to extrude than PTFE, PVDF is presently a more preferred fluoropolymer.

Intermediate tie layer 14 is interposed between outer layer 16 and core layer 12, preferably in a manner such that neither the inner or outer surface of intermediate tie layer 14 is exposed. Intermediate tie layer 14 is preferably made of a polymeric material comprising functionality capable of adhering outer layer 16 to core layer 12. In this manner, intermediate tie layer 14 aggressively links the two other layers together with a strong connection that resists delamination. Generally, preferred polymers for use in intermediate tie layer 14 have a weight average molecular weight in the range of from about 40,000 to about 250,000.

Additionally, due to the extreme difference in mechanical properties discussed above, intermediate tie layer 14 is preferably made of a material selected to have thermal

characteristics, e.g., a glass transition temperature, between those of core layer 12 and outer layer 16 so as to provide a step-wise transition in mechanical properties from the material of outer layer 16 to those of the material of core layer 12. Intermediate tie layer 14 thus operates to reduce the stresses that might otherwise be created as a result of the differing materials of outer layer 16 and core layer 12 if the intermediate tie layer 14 of the present invention were not used. By virtue of this relationship and the functionality of the material of the intermediate tie layer 14, layers 12, 14 and 16 are strongly adhered together in a manner resistant to delamination.

Thus, any polymer having a binding functionality capable of adhering to both core layer 12 and outer layer 16 may be advantageously used as intermediate tie layer 14. Representative examples of such polymers include olefinic and other free radically polymerized polymers having one or more functional groups selected from carbon-carbon double bonds, vinyl esters, amine groups, acid groups such as $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{PO}_3\text{H}$, the salts of such acids, and the like, an anhydric moiety such as



or combinations thereof, and the like.

For example, functionalized olefinic materials suitable for use in the intermediate tie layer 14 of tubing 10 include olefins such as polyethylene of varying densities, polypropylene, or polyethylene vinyl acetate that have been formed from olefinic monomers copolymerized with a copolymerizable monomer, e.g., maleic acid, having the desired functionality. Other unsaturated carboxylic acids such as fumaric acid, cinnamic acid, crotonic acid, linoleic acid, or the like may also be used as a substitute for maleic acid. These acid functional olefinic polymeric materials are described, for example, in U.S. Pat. No. 5,538,510, incorporated herein by reference.

Other examples of acid and anhydride functional polymers that are believed to be suitable for use in intermediate tie layer 14 include acid functional ethyl vinyl acetate resins, acid functional ethylene acrylate polymers, anhydride functional ethylene acrylate copolymers, anhydride functional ethyl vinyl acetate copolymers, acid and acrylate functional ethyl vinyl acetate resins, anhydride functional ethyl vinyl acetate copolymers, and anhydride functional ethyl vinyl acetate resins. In particular, suitable acid and anhydride functional polymers are commercially available under the trade name of Byne® from E.I. DuPont de Nemours, Wilmington, Del.

Functionalized polyethylenes are also suitable for use in intermediate tie layer 14. Examples of other such functionalized polyethylenes which are suitable for use in intermediate tie layer 14 include, but are not limited to, functionalized high density polyethylene and functionalized linear low density polyethylene. Such functionalized polyethylenes are commercially available from the Quantum Chemical Corporation under the trade name of Plexar®.

Additionally, the material of intermediate tie layer 14 may be a free radically polymerized copolymer of monomers comprising ethylene and an alkyl (meth)acrylate. Ethylene-methyl (meth)acrylate copolymers having ester functionality that are believed to be suitable as intermediate tie layer 14 are commercially available under the trade name EMAC® (e.g., EMAC® SP 2205 and 2260) from Chevron Company, Houston, Tex.

As mentioned hereinabove, the polymeric materials of the outer, core and intermediate tie layers 16, 12, and 14, respectively, are preferably comprised of materials with glass transition temperatures that are substantially similar so as to facilitate coextrusion and to help reduce the tendency of undue stress to build between the layers in the resultant tubing. Preferably, the glass transition temperature (T_g) of each layer will be from 85% to 115% of the glass transition temperature of the material(s) adjacent to it. In preferred embodiments, the T_g of the functionalized polymer of intermediate layer 14 is about 1 to 1.15 times greater than the polymer of outer layer 16, and the T_g of the lubricious polymer in core layer 12 is about 1 to 1.15 times greater than the functionalized polymer of intermediate tie layer 14.

Representative combinations of materials suitable for use in tubing 10 of the present invention are shown in Table 1, hereinbelow.

TABLE 1

| Core Layer (12) | Intermediate Tie Layer (14) | Outer Layer (16) |
|---------------------|-------------------------------|------------------|
| polyethylene | functionalized polyethylene | polyester |
| polyethylene | functionalized polyethylene | polyamide |
| polyethylene | ethylene-methyl acrylate | polyester |
| copolymers | ethylene-methyl acrylate | polyamide |
| polyethylene | ethylene-methyl acrylate | polyamide |
| copolymers | acid/anhydride functionalized | polyester |
| polyethylene | vinyl copolymer | polyester |
| fluorinated polymer | functionalized polyethylene | polyester |
| fluorinated polymer | functionalized polyethylene | polyamide |
| fluorinated polymer | ethylene-methyl acrylate | polyester |
| copolymers | ethylene-methyl acrylate | polyamide |
| fluorinated polymer | ethylene-methyl acrylate | polyamide |
| copolymers | acid/anhydride functionalized | polyester |
| fluorinated polymer | vinyl copolymer | polyester |

The thicknesses of layers 12, 14 and 16 will vary depending upon desired applications. For example, when used to define the guidewire lumen of an angioplasty catheter, the core layer 12 of tubing 10 will preferably have a thickness of from about 0.01 to about 0.05, while the intermediate tie layer 14 is preferably of a thickness of from about 0.006 to about 0.03 and outer layer 16 is preferably from about 0.01 to about 0.05 thick. More preferably, core layer 12 will be from about 0.01 to about 0.04 thick, intermediate tie layer 14 will be from about 0.003 to about 0.03 and outer layer 16 will be from about 0.01 mm to about 0.04.

Additionally, the diameter of tubing 10 will vary depending upon the end-use application. Typically, the overall, or outside, diameter (D_o) is typically between 0.5 and 0.7, and will preferably be from about 0.55 to about 0.63 mm. Core layer 12 will preferably define a lumen, such as a lumen adapted to receive a guidewire. The inside diameter (D_i) of the lumen so formed is typically from about 0.4 mm to about 0.6, and will preferably be from about 0.43 to about 0.51.

The tubing of the present invention may be used, for example, in medical devices suitable for percutaneous transluminal use, such as guide catheters, diagnostic catheters, or those medical devices in which a radially expansive component is to be therapeutically deployed, e.g., stent delivery devices or balloon catheters. In one embodiment of the invention, for example, the tubing of the present invention may be utilized to define a guidewire lumen in an over-the-wire balloon catheter 220, as illustrated in FIGS. 2 (where the balloon is illustrated in its deployed state), 3A, 3B and 3C. As illustrated, catheter 220 comprises an outer catheter tubing 222 which connects with balloon 224 at tubing distal end 226. Outer catheter tubing 222 terminates at its distal

end 226, where outer catheter tubing 222 connects with the proximal end 292 of balloon 224. Outer catheter tubing 222 defines lumen 294.

The aforementioned connection, and any other connection, weld or bond mentioned herein, may be established by any method that forms fluid tight seals between the materials at the desired bond site, e.g., as with adhesive, or by direct bonding. However, it is generally preferred that these connections be established by direct bonding. Direct bonding is considered advantageous since the use of an intermediate adhesive layer is thereby avoided. The use of adhesive is a less desirable alternative as adhesive layers add to the thickness and rigidity of the medical device at the bond site. Additionally, many adhesives present biocompatibility issues.

Thus, it is preferred that outer catheter tubing 222 is directly bonded to balloon 224 at distal end 226. These direct bonds may be established by any method known to those of ordinary skill in the art that effectively forms fluid tight seals between the materials to be bonded. For example, the direct bonds may be established by conductive, convective, or radiative heating, combinations thereof, of any one of these heating methods used in combination with pressure applied to the bond area. Furthermore, the direct bonds may be formed by fusion bonding. Fusion bonding using laser energy is disclosed in U.S. Pat. Nos. 5,267,959 and 5,501,759; the disclosures of which are incorporated by reference herein.

Also, catheter 220 comprises an inner catheter tubing 210 which defines lumen 234. Inner catheter tubing 210 extends through lumen 294 of outer catheter tubing 222, thus defining a generally annular space 230 between outer catheter tubing 222 and inner catheter tubing 210. Generally, annular space 230 extends along the catheter 220 between outer catheter tubing 222 and inner catheter tubing 210, to terminate in communication with the interior 296 of balloon 224. Inner catheter tubing 210, however, extends through balloon 224 as shown in FIG. 1, being bonded to balloon 224 at distal end 232 in such a manner that the lumen 234 of inner catheter tubing 210 is open at distal end 232. Advantageously and preferably, distal end 298 of inner catheter tubing 210 is directly bonded to balloon 224 at distal end 232.

Although inner catheter tubing 210 is in the form of trilayer tubing of the present invention as described hereinabove with respect to FIG. 1, the three layers have not been individually illustrated in FIG. 2 for purposes of clarity. As previously stated, the material of the core layer 12 (illustrated in FIG. 1) preferably comprises a lubricious material that defines a lubricious inner lumen. By providing a lubricious inner lumen, the advancement of catheter 220 over a guidewire or the advancement of a separate, smaller catheter, for example, through lumen 234 of tubing 210 is facilitated.

Because of the lubricious nature of the polymer of the core layer 12, the polymer that is to comprise outer layer 16 may be selected to optimize other characteristics of catheter 220 rather than to provide the necessary lubricity to the inner lumen of catheter 220. For example, the polymer of outer layer 16 may be chosen on the basis of bondability to the desired balloon material. In preferred embodiments, at least a portion of the monomeric segments of the polymer of outer layer 16 correspond to at least a portion of the monomeric segments of the desired balloon material. For example, if outer layer 16 comprises a polyether polyester, i.e., a polymer comprising polyester and polyether segments, it would be preferred that the balloon comprise a material with polyether or polyester segments, such as polyethylene terephthalate (PET).

In a second embodiment of the present invention, the trilayer, medical tubing of the present invention may be used as the inner catheter tubing 410 in a rapid exchange balloon catheter 420, as illustrated in FIGS. 4, 5A, 5B, and 5C. Again, although inner catheter tubing 410 is in the form of trilayer tubing of the present invention as described hereinabove with respect to FIG. 1, the three layers have not been individually illustrated in FIG. 4 for purposes of clarity.

Catheter 420 comprises a tubular proximal shaft 460, a tubular stem 462, inner catheter tubing 410 and a balloon 424. Stem 462 is in fluid communication with proximal shaft 460 and is bonded to the distal end 492 of proximal shaft 460. Inner catheter tubing 410 defines guidewire lumen 434. Inner catheter tubing 410 extends from distal portion 492 of proximal shaft 460 and through lumen 464 of stem 462, beyond the distal end 494 of stem 462, and through balloon 424. Inner catheter tubing 410 additionally comprises a proximal end 496 open to the outside of the catheter 420 at skive 466. Inner catheter tubing 410 and stem 462 are preferably directly bonded together at weld 4102 proximal to balloon 424. At the skive 466, the distal end 492 of proximal shaft 460, the proximal end 496 of tubular stem 462, and the proximal end 4100 of inner catheter tubing 410 are directly bonded together. Inner catheter tubing 410 is off-center at skive 466 but becomes approximately centered throughout the remaining length of stem 462. Balloon 424 is arranged coaxially around inner catheter tubing 410 with the proximal neck 4104 of balloon 424 directly bonded to the distal end of stem 462 at the outer surface thereof. The distal neck 432 of balloon 424 is directly bonded to the distal end 4106 of inner catheter tubing 410, together forming the catheter tip 468.

In a third embodiment of the present invention, the tubing of the present invention may be used as the inner member 710 in a stent delivery device, as illustrated in FIG. 7, in which the stent is illustrated in its deployed state. As was the case with FIGS. 2 and 4, although inner catheter tubing 710 is in the form of trilayer tubing of the present invention as described hereinabove with respect to FIG. 1, the three layers have not been individually illustrated in FIG. 7 for purposes of clarity.

Stent delivery device 720 comprises a tubular outer sleeve 722 and a hollow, flexible core element 710. Outer sleeve 722 has integral handle 734 attached at its proximal end. The distal end 724 of outer sleeve 722 is positioned within a body canal 738. Disposed axially within outer sleeve 722 is hollow, flexible core element 710 having a handle 736 at its proximal end. The distal end 728 of the core element 710 has a stepped up diameter where it meets the distal end 724 of outer sleeve 722 so that it provides a smooth transition at the distal end 724 of outer sleeve 722, and is also located within body canal 738. A guide wire 730 passes axially through the hollow core. Attached around the periphery of the core element 710 at its distal end 728 is grip member 732 which releasably grips a self-expanding stent 726 (shown partly deployed).

The tubing 10 of the present invention can be manufactured by coextrusion as schematically illustrated in FIG. 6. Although three extruders typically are used, one for each layer 12, 14 and 16, only one extruder 605 is shown for purposes of clarity. In the case of such trilayer extrusion, the three desired materials can converge through one die 646 to create a single trilayer tube. Referring to the operation of extruder 605, which is representative of all three extruders, pellets (not shown) of suitable material can be gravitationally fed from a hopper 640 into the feed section 654 of extruder 605. There, the pellets come into contact with

rotating screw 656. The pellets are then conveyed through barrel 658 by rotating screw 656. The pellets are heated by electrically heated barrel 658 and by the frictional and shear action of the screw 656 as it turns in the barrel 658. Eventually, as the pellets move down the length of the barrel 658, the pellets are transformed into a molten phase which is then forced out of a coextrusion die 646 along with molten material from the other two extruders to create a coextruded tube 660. The tube 660 is then drawn down into cooling trough 648 to cool and set the tube 660 into a predetermined thickness and diameter by means of puller 650. Once the tube 660 is cooled and pulled it is ready for collection, i.e., with a cutter (not shown) or coiler 652, and use.

For example, the extrusion line may comprise the following equipment:

- 2 ¾" Davis Standard Extruder (for inner and outer layers)
 - 1 ½-¾" Davis Standard Extruder (for middle layer)
 - 1 3-layer Genca Crosshead (tri-die, commercially available from Genca Extrusion Technology, Clearwater, Fla.)
 - 1 Water Bath
 - 1 Puller RDN
 - 1 Laser gauge Zumbach (to check dimensions).
- Process conditions include:

| | |
|--------------|---------------|
| Temperatures | 370°-470° F. |
| Pressures | 1000-3000 psi |
| Line Speed | 50-200 fpm |

The following examples, while not intended to be limiting, illustrate various features of the present invention.

EXAMPLE 1

The following experiment was performed to investigate the effects of irradiation sterilization on an HDPE layer of trilayer tubing.

Specifically, one hundred pieces of 6" tubing made of Hytrel® 63D as the outside layer, Plexar® 209 as the middle layer, and HDPE 6007 as the inside layer were irradiated (0.0185" overall ID×0.0265" overall OD). Twenty pieces were irradiated at dosages of 20 Mrad, 30 Mrad, 40 Mrad, 50 Mrad, and 60 Mrad, respectively. Control samples receiving no irradiation were also provided.

Differential Scanning Calorimetry (DSC) was used to determine the thermal properties of the three different layers.

No significant differences were seen between control samples or samples at any of the dosage levels.

Solids rheology testing was also performed with similar conclusions. No significant changes were detected between the samples at any of the dosage levels.

To test the effect of the irradiation on the bondability of the outer surface of the tubing to balloon material, PET balloons were bonded to the tubing by fusion bonding and then the bond site skived and inspected for delamination. No significant differences in the amount of delamination were noted between any of the dosage levels and the control.

It was concluded that irradiating with electron-beam irradiation the trilayer tubing does not adversely affect resistance to delamination nor does irradiation increase the melt resistance of the HDPE layer.

EXAMPLE 2

Tests were performed to determine if trilayer tubing can be effectively laser-bonded to angioplasty balloons comprising polyethyleneterephthalate (PET) as an inner balloon layer. Trilayer tubing having an inner diameter (ID) of 0.0182 inches and an outer diameter (OD) of 0.0236 inches and including Hytrel® 7246 as the outside layer, Plexar® 209 as the middle layer, and HDPE 5006 as the inside layer, was tested.

The outer layer of the tubing was fusion bonded to PET of balloon using laser energy as described in Forman, U.S. Pat. No. 5,501,759. Weld spot size was held constant at 2.215 inches and RPM was held constant at 2500. Power was varied between 2.0, 3.0, and 4.0 Watts, respectively.

It was concluded that effective bonds were achieved at all power levels. No bonds failed before balloon burst occurred. Also, times for proximal and distal bonds were set for each power level, despite the variation in wall thickness between parts. The best bonds were achieved with the 3.0 Watt power setting, based on visual examination after burst.

EXAMPLE 3

Crush tests were performed on tubing of the present invention made of Hytrel® 7246 as the outside layer, Plexar® 209 as the middle layer, and HDPE 6007 as the inside layer.

| Start Pressure: 147.0 (10 ATM) Increment: 14.7 PSI | | | | Stop Pressure: 411.6 (28 ATM) Hold Time: 15 seconds | | | |
|---|--------|-------------------|------------------|--|---------------------------|----------|---------|
| | | RESISTANCE | LOCKS | DAMAGE | AFTER INFLATION TO 28 ATM | | |
| ID* | OD* | FELT AT: | UP AT: | OBSERVED | AVG OD* | MIN. OD* | MAX OD* |
| 0.0169 | 0.0225 | 352.8 (24 ATM) | Does Not Lock | No Damage | 0.0226 | 0.0224 | 0.0227 |
| 0.0169 | 0.0224 | 367.5 (24 ATM) | Does Not Lock | No Damage | 0.0227 | 0.0226 | 0.0228 |
| 0.0172 | 0.0232 | 352.8 (24 ATM) | Does Not Lock | No Damage | 0.0231 | 0.0228 | 0.0234 |
| 0.0169 | 0.0226 | 382.2 (26 ATM) | Does Not Lock | No Damage | 0.0228 | 0.0226 | 0.0229 |
| 0.017 | 0.0227 | 367.5 (25 ATM) | Does Not Lock | No Damage | 0.0228 | 0.0225 | 0.023 |

-continued

| Start Pressure: 147.0 (10 ATM) Increment: 14.7 PSI | | | | Stop Pressure: 411.6 (28 ATM) Hold Time: 15 seconds | | | |
|---|-----------------------|-------------------------|--------|--|------------------------|------------------------|------------------------|
| RESISTANCE | | LOCKS | | DAMAGE <u>AFTER INFLATION TO 28 ATM</u> | | | |
| ID* | OD* | FELT AT: | UP AT: | OBSERVED | AVG OD* | MIN. OD* | MAX OD* |
| x = .0170 s = .0001 | x = .023 s = .0003 | x = 364.56 s = 12.30 | | | x = .0228 s = .0002 | x = .0226 s = .0001 | x = .0230 s = .0003 |

x = mean.

s = standard deviation.

"Resistance felt" means the point when the tube collapsed enough so that an increase in friction was felt on a guidewire by an operator pulling it through the tubing. "Locks up" is meant to indicate the point at which the guidewire is completely stuck due to the collapse of the tube.

EXAMPLE 4

Crush tests were performed on tubing of the present invention made of Hytrel® 7246 as the outside layer, Plexar® 209 as the middle layer, and HDPE 6007 as the inside layer.

| Start Pressure: 147.0 (10 ATM) Increment: 14.7 PSI | | | | Stop Pressure: 411.6 (28 ATM) Hold Time: 15 seconds | | | |
|---|-----------------------|------------------------|------------------------|--|---------------------------|------------------------|---------|
| | | RESISTANCE | LOCKS | DAMAGE | AFTER INFLATION TO 28 ATM | | |
| ID* | OD* | FELT AT: | UP AT: | OBSERVED | AVG OD* | MIN. OD* | MAX OD* |
| 0.0169 | 0.0228 | 367.5 (25 ATM) | 470.4 (32 ATM) | Slightly Oval | 0.0228 | 0.0224 | 0.0232 |
| 0.0168 | 0.0232 | 382.2 (26 ATM) | 470.4 (32 ATM) | Slightly Oval | 0.0228 | 0.0226 | 0.023 |
| 0.0171 | 0.0235 | 382.2 (26 ATM) | 470.4 (32 ATM) | Slightly Oval | 0.0232 | 0.0225 | 0.0235 |
| 0.0168 | 0.0227 | 367.5 (25 ATM) | 455.7 (31 ATM) | Slightly Oval | 0.0226 | 0.0222 | 0.023 |
| 0.0171 | 0.023 | 367.5 (25 ATM) | 470.4 (32 ATM) | Slightly Oval | 0.0228 | 0.0223 | 0.0231 |
| x = .0169 s = .0002 | x = .023 s = .0003 | x = 373.38 s = 8.05 | x = 467.46 s = 6.57 | x = .0228 s = .0002 | x = .0224 s = .0002 | x = .0232 s = .0002 | |

x = mean.

s = standard deviation.

"Resistance felt" and "lock-up" have the same meanings as in Example 3.

EXAMPLE 5

Tests were performed to determine the tensile strength effect of annealing at different temperatures and times for 0.0185" IDx0.0235" OD trilayer tubing. Material composition of the tubing is Hytrel® 7246 as the outside layer, Plexar® 209 as the middle layer, and HDPE 6007 as the inside layer. Five unannealed tubes of the same size were tested and found to have an average peak load of 1.255 lbs (standard deviation 0.047).

-continued

| Annealing time, temp | Peak Load lb. | Peak Stress psi | % Strain @ Break % | Yield Stress psi | % Strain @ yield % | Modulus psi |
|----------------------|---------------|-----------------|--------------------|------------------|--------------------|-------------|
| 2.5 hr., 110° C. | 1.4 | 8728.6 | 385.7 | 4710.7 | 11.694 | 96051.8 |
| 1 hr., 120° C. | 1.5 | 9041.8 | 389.2 | 4885.3 | 12.682 | 96250.6 |
| 4 hr., 120° C. | 1.6 | 9421.3 | 382.3 | 4954.6 | 12.131 | 96887.6 |

EXAMPLE 6

A test was performed on 10 pieces measuring 0.0185" IDx0.0235" OD to check for shrinkage. The pieces were made of Hytrel® 7246 as the outside layer, Plexar® 209 as the middle layer, and HDPE 6007 as the inside layer. Parts were measured for i.d. with a mandrel, o.d. in two marked places, and length. They were annealed for 4 hours at 120°

C. and found to have no significant shrinkage in any parameter measured.

In sum, it has been found that medical tubing made according to the present invention allowed for good guidewire movement (with or without blood in lumen), traceability, ability to bend, crush resistance, kink resistance, low profile, good tensile strength, costability, cost effectiveness, gamma stability, and biocompatibility.

Other embodiments of this invention will be apparent to those skilled in the art upon consideration of this specification or from practices of the invention disclosed herein. Various omissions, modifications, and changes to the principles and embodiments described herein may be made by one skilled in the art without departing from the true scope and spirit of the invention which is indicated by the following claims. For instance, additional layers (e.g., a fourth layer) can be extruded inside of the inner layer or outside of the outer layer. All documents cited herein are incorporated by reference in their entireties for all purposes.

What is claimed is:

1. A co-extrusion of polymeric materials, the co-extrusion comprising:

a first polymeric material having a first glass transition temperature;

a second polymeric material having a second glass transition temperature; the second polymeric material further lacking a bonding affinity with the first polymeric material;

an intermediate layer having a third glass transition temperature, the intermediate layer positioned between the first polymeric material and the second polymeric material, the intermediate layer further having a bonding affinity to both the first polymeric material and the second polymeric material; and

wherein the glass transition temperatures for the first polymeric material, the second polymeric material, and the intermediate layer are within 85% to 115% of one another.

2. The co-extrusion of claim 1, wherein the co-extrusion is tubular in shape.

3. The co-extrusion of claim 2, wherein the first polymeric material defines a lumen of the tubular co-extrusion.

4. The co-extrusion of claim 1, wherein the second polymeric material is selected from a polyester, a polyamide, or combinations thereof.

5. The co-extrusion of claim 1, wherein the second polymer is a polyester.

6. The co-extrusion of claim 5, wherein the polyester comprises at least one polyether segment and at least one polyester segment.

7. The co-extrusion of claim 1, wherein the second polymer is a polyamide.

8. The co-extrusion of claim 1, wherein the first polymeric material is selected from an olefinic polymer, a fluorinated polymer or combinations thereof.

9. The co-extrusion of claim 8, wherein the olefinic polymer is selected from high density polyethylene, ultra high density polyethylene, low density polyethylene, linear low density polyethylene, or combinations thereof.

10. The co-extrusion of claim 8, wherein the fluorinated polymer is polyvinylidene fluoride.

11. The co-extrusion of claim 1, wherein the intermediate tie layer comprises a polymer selected from an anhydride modified olefinic polymer, an acrylate modified olefinic polymer, or combinations thereof.

12. The co-extrusion of claim 11, wherein the polymer of the intermediate tie layer is selected from a functionalized

polyethylene, a functionalized vinylic polymer, a ethylene-methyl acrylate copolymer, an acid modified ethyl vinyl acetate polymer, an acid modified ethylene acrylate copolymer, an anhydride modified ethylene acrylate copolymer, an anhydride modified ethyl vinyl acetate copolymer, an acid modified ethyl vinyl acetate polymer, an acrylate modified ethyl vinyl acetate polymer, an anhydride modified ethyl vinyl acetate copolymer, an anhydride modified ethyl vinyl acetate polymer, or combinations thereof.

13. The co-extrusion of claim 12, wherein the polymer of the intermediate tie layer is selected from a functionalized polyethylene, a functionalized copolymer obtained from monomers comprising ethylene and allyl (meth)acrylate, an anhydride modified ethyl vinyl acetate polymer, or combinations thereof.

14. A catheter shaft for percutaneous transluminal use, the catheter shaft comprising:

an outer layer having a first glass transition temperature;

a core layer defining a lumen extending the length therethrough, the core layer having a third transition temperature; and

an intermediate tie layer disposed between at least a portion of the outer layer and the core layer, the intermediate tie layer having a second glass transition temperature; and

wherein the first, the second and the third glass transition temperatures are within 85% to 115% of the glass transition of the layer or layers adjacent thereto.

15. The catheter shaft of claim 14, wherein the outer layer lacks a bonding affinity to the core layer.

16. The catheter shaft of claim 14, wherein the intermediate tie layer possesses a bonding affinity to both the outer layer and the core layer.

17. The catheter shaft of claim 14, wherein the catheter shaft further comprises a radially expansive component coupled to the catheter shaft.

18. The catheter shaft of claim 17, wherein the radially expansive component is a balloon.

19. The catheter shaft of claim 14, wherein the outer layer is selected from a polyester, a polyamide, or combinations thereof.

20. The catheter shaft of claim 14, wherein the core layer is selected from an olefinic polymer, a fluorinated polymer or combinations thereof.

21. A balloon catheter for percutaneous transluminal use, the balloon catheter comprising:

a first tubular member having a lumen extending the length therein;

a second tubular member coaxially disposed within at least a portion of the first tubular member with a distal segment extending distally beyond a distal end of the first tubular member, wherein the second tubular member comprises a core layer having a first glass transition temperature, an outer layer having a third glass transition temperature, and an intermediate tie layer disposed between at least a portion of the outer layer and the core layer, the intermediate tie layer having a second glass transition temperature, wherein the first glass transition temperature is greater than the second glass transition temperature, and the second glass transition temperature is greater than the third glass transition temperature, and further wherein the first glass transition temperature, the second glass transition temperature and the third glass transition temperatures are within 85% to 115% of the glass transition temperature of the layer or layers adjacent thereto; and

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a balloon having a proximal end, a distal end and an expandable region there between, wherein the distal end of the balloon is affixed to the distal segment of the second tubular member and the proximal end of the balloon is affixed to the first tubular member, and further wherein the expandable region of the balloon is in fluid communication with the lumen of the first tubular member.

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22. The balloon catheter of claim 21, wherein the outer layer is selected from a polyester, a polyamide, or combinations thereof.

23. The balloon catheter of claim 22, wherein the core layer is selected from an olefinic polymer, a fluorinated polymer or combinations thereof.

* * * * *

(12) **United States Patent**
Böer et al.

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(54) **MULTILAYER COMPOSITE**

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(57) **ABSTRACT**

A thermoplastic multilayer composite, and articles made therefrom, which has at least one layer I of a thermoplastic molding composition, at least one layer II of a further thermoplastic molding composition, bonded together with at least one layer of an adhesion promoter disposed between at least one layer I and at least one layer II. The adhesion promoter is at least 5% by weight of a graft copolymer prepared from 0.5 to 25% by weight, based on the total amount of graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, and polyamide-forming monomers selected from lactams, ω -aminocarboxylic acids, equimolar mixtures of diamines and dicarboxylic acids, and their mixtures.

31 Claims, No Drawings

MULTILAYER COMPOSITE

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to an adhesion promoter for a multilayer composite, and to a multilayer composite which contains this adhesion promoter.

Individual polymers such as polyamides or polyesters are unsuitable for many applications. For example, polyamides are not resistant to weathering since they age upon exposure to the UV radiation from sunlight, extremes of heat and cold, and can absorb atmospheric moisture. This results in discoloration, impairment of the mechanical properties and warping phenomena. In addition, although polyamides have good mechanical properties, particularly good toughness, they provide a poor barrier to the diffusion of molecules: polar substances in particular can easily diffuse through polyamides. Thus, polyamides are unsuitable for use in fuel lines in which alcohol-containing fuel is conveyed, because the alcohol component of the fuel can easily diffuse through the polyamide.

Polyesters generally have good weathering resistance and provide an excellent barrier to the diffusion of both polar and non-polar molecules. However, polyesters are generally impact-sensitive; the notched impact strength of polyesters in particular is frequently inadequate for many applications. Polyesters therefore cannot be used by themselves in many applications in which their other properties, such as their excellent barrier properties, high heat resistance and good rigidity, would be desired.

Similarly, other polymers also exhibit a mix of desirable and undesirable properties such as those described for polyamides and polyesters, and are consequently unsuitable for many applications.

If various polymers could be strongly bonded into laminated articles, it would be possible to combine the complementary properties of various polymers in order to form articles which exhibit some of the best properties of each of the polymer employed. For example, it may be possible to protect polyamide moldings against light and humidity (i.e., weathering) by coating them with a polyester. Similarly, polyester moldings could be weathering) by coating them with a polyester. Similarly, polyester moldings could be protected against chemical and mechanical attack by coating them with a polyamide. Thus, if different polymers could be strongly bonded together, it would be possible to provide articles such as fuel lines, which usually consist of a polyamide (PA), such as PA 6, PA 11 or PA 12 (i.e., poly(ω -amino-caproic acid), poly(ω -amino-undecanoic acid), poly(ω -amino-dodecanoic acid), respectively), with a barrier layer to fuel, in particular to alcohol-containing fuel. In addition, such laminates comprising various layers of different polymers having different functions are more suitable than monolayers for food packaging.

Composites of polyamides and polyesters are already known in principle. EP-A-0 336 806 describes the coextrusion of PA 12 and polybutylene terephthalate (PBT) to give a two-layer pipe. German Patent 37 27 092 describes a multilayer pipe which has, from the inside outward, layers of polyamide, polyvinyl alcohol, polyamide and polyester. However, it is well known that the majority of polymers, including polyamides and polyesters, are incompatible with one another, which is why adhesion is poor between the laminate layers of polymer laminates. However, a strong bond between the individual polymer layers is absolutely necessary in conventional industrial applications.

DE-A 196 33 133 describes a multilayer pipe comprising at least two layers bonded well to one another, where the first layer is a barrier layer and the thermoplastic of the second layer has been treated with polyethyleneimine as adhesion promoter. However, when this process was repeated, the desired bonding did not occur.

A typical approach to bonding, for example polyester and polyamide layers, would be to use an adhesion promoter consisting of a mixture of polyamide and polyester. However, blends of this type, which are usually prepared by mixing the melts in an extruder, are very brittle. Corresponding coextrusion experiments in which the polyamide and polyester are bonded with such polyamide/polyester blend adhesion promoters either exhibit adhesion of the adhesion promoter to the polyamide or to the polyester, but never to both of the two polymers simultaneously.

EP-A-0 509 211 describes thermoplastic multilayer composites in which a layer of a polyamide molding composition and a layer of a polyester molding composition are bonded by means of an adhesion promoter which comprises a mixture of polyamide and polyester. Since the problems discussed above occur here, in a preferred embodiment at least part of the polyamide content and of the polyester content in the adhesion promoter are in the form of a polyamide-polyester block copolymer. However, the preparation of polyamide-polyester block copolymers of this type is not easy and requires the addition of auxiliaries or catalysts. Furthermore, because the block copolymers are prepared by linking suitable end groups of polyamide and/or polyester polymers, precise control of the end groups is necessary in order to ensure that the appropriate end groups are present in sufficient concentration. Since commercial grades of polyamide or polyester polymers do not meet these requirements, specially grades of these polymers must be prepared and subsequently converted into a block copolymer. The production of adhesion promoters of this type therefore requires considerable effort. This is more particularly true of the block copolyester-amides employed in the process of EP-A-0 837 088 as adhesion promoters in polyamide-polyester multilayer composites.

Composites comprising other materials are also known, but due to the abovementioned incompatibility of most polymer materials, similar types of individually matched adhesion promoters are usually required.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an inexpensive, easy-to-prepare, but nonetheless effective adhesion promoter for a multilayer composite. In a multilayer composite of this type, the layer adhesion should be maintained for a long time, even in contact with reagents such as, for example, fuel, solvents, oil or greases and at elevated temperatures.

This object has been achieved by a thermoplastic multilayer composite comprising at least one layer I of a thermoplastic molding composition, at least one layer II of a further thermoplastic molding composition and, in between layer I and layer II, a layer of an adhesion promoter which comprises at least 5% by weight, preferably at least 10% by weight and particularly preferably at least 20% by weight of a graft copolymer prepared using the following monomers:

- from 0.5 to 25% by weight, preferably from 1 to 20% by weight and particularly preferably from 1.5 to 16% by weight, based on the graft copolymer, of a polyamine having at least 4, preferably at least 8 and particularly preferably at least 11 nitrogen atoms and

having a number average molecular weight M_n of at least 146 g/mol, preferably of at least 500 g/mol and particularly preferably of at least 800 g/mol, and

- b) polyamide-forming monomers selected from lactams, ω -aminocarboxylic acids and/or equimolar combinations of diamine and dicarboxylic acid.

DETAILED DESCRIPTION OF THE INVENTION

The polyamine component of the graft copolymer can be, for example, the following classes of polyamines:

polyvinylamines (Römpf Chemie Lexikon {Römpf's Lexicon of Chemistry}, 9th Edition, Volume 6, page 492f, Georg Thieme Verlag, Stuttgart, 1992);

polyamines prepared from alternating polyketones (DE-A 196 54 058);

dendrimers, such as, for example, $(H_2N-(CH_2)_3)_2N-(CH_2)_3-N(CH_2)_3-N(CH_2)_3-NH_2$ (DE-A-196 54 179) or tris(2-aminoethyl)amine, N,N -bis(2-aminoethyl)- N' , N' -bis{2-[bis(2-aminoethyl)amino]ethyl}-1,2-ethanediamine or 3,15-bis(2-aminoethyl)-6,12-bis{2-[bis(2-aminoethyl)amino]ethyl}-9-[2-[bis{2-bis(2-aminoethyl)amino]ethyl}amino]ethyl}-3,6,9,12,15-pentazaoheptadecane-1,17-diamine (J. M. Warakomski, Chem. Mat. 1992, 4, 1000-1004);

linear polyethyleneimines, which can be prepared by polymerization of 4,5-dihydro-1,3-oxazoles followed by hydrolysis (Houben-Weyl, Methoden der Organischen Chemie {Methods of Organic Chemistry}, Volume E20, pages 1482-1487, Georg Thieme Verlag, Stuttgart, 1987);

branched polyethyleneimines, which are obtainable by polymerization of aziridines (Houben-Weyl, Methoden der Organischen Chemie {Methods of Organic Chemistry}, Volume E20, pages 1482-1487, Georg Thieme Verlag, Stuttgart, 1987) and which generally have the following amino group distribution: from 25 to 46% of primary amino groups, from 30 to 45% of secondary amino groups and from 16 to 40% of tertiary amino groups.

In the preferred case, the polyamine has a number average molecular weight M_n of at most 20,000 g/mol, particularly preferably of at most 10,000 g/mol and especially preferably of at most 5000 g/mol.

Lactams and ω -aminocarboxylic acids which are employed as polyamide forming monomers contain from 4 to 19 and in particular from 6 to 12 carbon atoms. In addition, the number of carbon atoms of the polyamide forming monomers may be 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, and 18 carbon atoms, inclusive of all subranges therebetween. Particular preference is given to ϵ -caprolactam, ϵ -aminocaproic acid, caprylactam, ω -aminocaprylic acid, lauro lactam, ω -aminododecanoic acid and/or ω -aminoundecanoic acid.

Combinations of diamine and dicarboxylic acid are, for example, hexamethylenediamine/adipic acid, hexamethylenediamine/dodecanedioic acid, octamethylenediamine/sebacic acid, decamethylenediamine/sebacic acid, decamethylenediamine/dodecanedioic acid, dodecamethylenediamine/dodecanedioic acid and dodecamethylenediamine/2,6-naphthalenedicarboxylic acid. In addition, however, it is also possible to employ all other combinations, such as decamethylenediamine/dodecanedioic acid/terephthalic acid,

hexamethylenediamine/adipic acid/terephthalic acid, hexamethylenediamine/adipic acid/caprolactam, decamethylenediamine/dodecanedioic acid/ ω -aminoundecanoic acid, decamethylenediamine/dodecanedioic acid/lauro lactam, decamethylenediamine/terephthalic acid/lauro lactam or dodecamethylenediamine/2,6-naphthalenedicarboxylic acid/lauro lactam.

In a preferred embodiment, the graft copolymer is prepared with the additional use of an oligocarboxylic acid selected from 0.015 to about 3 mol % of dicarboxylic acid and/or 0.01 to about 1.2 mol % of tricarboxylic acid, in each case based on the sum of the moles of the polyamide-forming monomers. In this connection, each monomer in the equivalent combination of diamine and dicarboxylic acid is considered individually. If a dicarboxylic acid is used, preferably from 0.03 to 2.2 mol %, particularly preferably from 0.05 to 1.5 mol %, very particularly preferably from 0.1 to 1 mol % and in particular from 0.15 to 0.65 mol % is added. If a tricarboxylic acid is used, preferably from 0.02 to 0.9 mol %, particularly preferably from 0.025 to 0.6 mol %, very particularly preferably from 0.03 to 0.4 mol % and in particular from 0.04 to 0.25 mol % is used. The concomitant use of the oligocarboxylic acid significantly improves the solvent and fuel resistance, in particular the hydrolysis and alcoholysis resistance and the stress cracking resistance, but also the swelling behavior and consequently the dimensional stability, as well as the diffusion barrier action.

The oligocarboxylic acid employed can be any desired di- or tricarboxylic acid having 6 to 24 carbon atoms, for example adipic acid, sebacic acid, azelaic acid, sebacic acid, dodecanedioic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid, trimelic acid and/or trimellitic acid. In addition the oligocarboxylic acid can have 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, or 23 carbon atoms, inclusive of all subranges therebetween.

If desired, aliphatic, alicyclic, aromatic, alkyl and/or alkaryl-substituted monocarboxylic acids having 3 to 50 carbon atoms, such as, for example, lauric acid, unsaturated fatty acids, acrylic acid or benzoic acid, can be employed as a regulator. By means of these regulators, the concentration of amino groups can be reduced without changing the shape of the molecule. In addition, functional groups, such as those containing double or triple bonds, etc., can be introduced in this way. However, it is desired that the graft copolymer has a substantial content of amino groups. The amino group concentration of the graft copolymer is preferably in the range from 150 to 1500 mmol/kg, particularly preferably in the range from 250 to 1300 mmol/kg and very particularly preferably in the range from 300 to 1100 mmol/kg. Here and below, the term "amino groups" is taken to mean not only amino end groups, but also any secondary or tertiary amino groups which may be present in the polyamine.

In a preferred embodiment, the amino group concentration of the graft copolymer is in the range from 100 to 2500 mmol/kg, including 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, and 2400 mmol/kg, inclusive of all values and subranges therebetween.

The graft copolymers according to the invention can be prepared by various processes. One method is to initially introduce the lactam or ω -aminocarboxylic acid and polyamine together and to carry out the polymerization or polycondensation. The oligocarboxylic acid can be added either at the beginning or during the reaction.

However, a preferred process comprises, in a two-step process, first carrying out the lactam cleavage and prepoly-

merization in the presence of water (alternatively, the corresponding ω -aminocarboxylic acids or diamines and dicarboxylic acids are employed and prepolymerized directly). Second, the polyamine is added, while any oligocarboxylic acid used concomitantly is metered in before, during or after the prepolymerization. The mixture is then polycondensed at temperatures of from 200 to 290° C. in a stream of nitrogen or under reduced pressure.

A further preferred process comprises the hydrolytic degradation of a polyamide to a prepolymer and the simultaneous or subsequent reaction with the polyamine. Preference is given to polyamides in which the end group difference is approximately zero or in which any oligocarboxylic acid used concomitantly has already been copolycondensed. However, the oligocarboxylic acid can also be added at the beginning or during the degradation reaction.

These processes allow the preparation of ultra-highly branched polyamides having acid numbers of less than 40 mmol/kg, preferably less than 20 mmol/kg and particularly preferably less than 10 mmol/kg. After a reaction time of only from one to five hours at temperatures of from 200° C. to 290° C., approximately complete conversion is achieved.

If desired, the above ultra-highly branched polyamides may be treated for a period of hours under vacuum. This vacuum treatment lasts at least four hours, preferably at least six hours and particularly preferably at least eight hours at from 200 to 290° C. After an induction period of several hours, an increase in the melt viscosity is then observed, which is probably due to the reaction of amino end groups with one another, together with elimination of ammonia and chain extension and/or cross-linking. This further increases the molecular weight, which is particularly advantageous for extrusion molding compositions. Alternatively, the ultra-highly branched polyamide can also be post-condensed as a solid rather than a melt.

By means of the above-described adhesion promoter, a multiplicity of polymers or molding compositions based thereon can be bonded to one another. In general, suitable polymers are all those which, owing to structural similarities, are physically compatible with the graft copolymer of this invention, such as, for example, polyamides. Equally suitable are all polymers which undergo some sort of chemical linking reaction, for example, polymers which chemically react with or at least form hydrogen bonds with the amino groups of the graft copolymer, such as, for example, polyesters.

Embodiments according to the invention are, for example:

A multilayer composite which comprises layers of different polyamide molding compositions which are of low compatibility or are incompatible with one another and which are bonded by means of the adhesion promoter according to the invention.

A multilayer composite which comprises layers of different polyester molding compositions which are incompatible with one another and are bonded by the adhesion promoter according to the invention.

A multilayer composite which comprises a layer of a polyamide molding composition which is bonded, by means of the adhesion promoter according to the invention, to a layer of another molding composition which is based on a polymer which is not a polyamide.

A multilayer composite which comprises a layer of a polyester molding composition which is bonded, by means of the adhesion promoter according to the invention, to a layer of another molding composition which is based on a polymer which is not a polyester.

A multilayer composite which comprises the following layers:

I. A layer I of a polyamide molding composition;

II. A layer II of a polyester molding composition; and between layer I and layer II, a layer of the adhesion promoter according to the invention.

Suitable polyamides are primarily aliphatic homo- and copolycondensates, for example PA 46, PA 66, PA 68, PA 612, PA 88, PA 810, PA 1010, PA 1012, PA 1212, PA 6, PA 7, PA 8, PA 9, PA 10, PA 11 and PA 12. (The notation of the polyamides corresponds to the international standard, where the first number(s) indicates the number of carbon atoms in the starting diamine and the final number(s) denotes the number of carbon atoms in the dicarboxylic acid. If only one number is given, this means that the starting material was an α , ω -aminocarboxylic acid or the lactam derived therefrom; for more information, see H. Dominigshaus, Die Kunststoffe und ihre Eigenschaften [The Plastics and Their Properties], pages 272 ff., VDI-Verlag, 1976.)

If copolyamides are used, these can contain, for example, adipic acid, sebacic acid, suberic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, etc., as co-acid or bis(4-aminocyclohexyl)methane, trimethylhexamethylenediamine, hexamethylenediamine or the like as co-diamine. Lactams, such as caprolactam or laurolactam, or aminocarboxylic acids, such as ω -aminoundecanoic acid, can likewise be incorporated as co-components. The preparation of these polyamides is known (for example D. B. Jacobs, J. Zimmermann, Polymerization Processes, pp. 424-467, Interscience Publishers, New York, 1977; DE-B 21 52 194).

In addition, suitable polyamides are also mixed aliphatic/aromatic polycondensates, as described, for example, in U.S. Pat. Nos. 2,071,250, 2,071,251, 2,130,523, 2,130,948, 2,241,322, 2,312,966, 2,512,606 and 3,393,210, and in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 18, pages 328 ff. and 435 ff., Wiley & Sons, 1982. Other suitable polyamides are poly(ether-ester-amides) and poly(ether-amides); products of this type are described, for example, in DE-A 25 23 991, 27 12 987 and 30 06 961.

The polyamide molding composition can comprise either one of these polyamides or a plurality of polyamides in the form of a mixture. Furthermore, up to 40% by weight of other thermoplastics may be present so long as they do not adversely affect the bonding ability; in particular impact-modifying rubbers, such as ethylene-propylene or ethylene-propylene-diene copolymers (EPA-0 295 076), polybutadiene, polyoctadiene, random or block copolymers of alkenyl-aromatic compounds with aliphatic olefins or dienes (EP-A-0261 748) or core/shell rubbers having a tough, elastic core of (meth)acrylate, butadiene or styrene-butadiene rubber having glass transition temperatures (T_g) of <-10° C., where the core may be crosslinked and the shell may be built up from styrene and/or methyl methacrylate and/or further unsaturated monomers (DE-A 21 44 528 and 37 28 685).

The conventional auxiliaries and additives for polyamides, such as, for example, flame retardants, stabilizers, plasticizers, processing auxiliaries, fillers, in particular fillers which improve the electrical conductivity, reinforcing fibers, pigments or the like, can be added to the polyamide molding composition. The amount of said agents should be metered in such a way that the desired properties are not seriously impaired.

Suitable polyesters are thermoplastic polyesters having a linear structure. These are prepared by polycondensation of diols with dicarboxylic acid or polyester-forming derivatives thereof, such as dimethyl esters. Suitable diols have the formula HO—R—OH, where R is a divalent, branched or

unbranched, aliphatic and/or cycloaliphatic radical having 2 to 40, preferably 2 to 12, carbon atoms. Suitable dicarboxylic acids have the formula $\text{HOOC}-\text{R}'-\text{COOH}$, where R' is a divalent aromatic radical having 6 to 20, preferably 6 to 12, carbon atoms.

Examples of diols which may be employed are ethylene glycol, trimethylene glycol, tetramethylene glycol, hexamethylene glycol, neopentyl glycol, cyclohexanedimethanol and the C_{30} -diol diester diol. The diols can be employed alone or as a diol mixture.

Up to 25 mol % of said diol may be replaced by a polyalkylene glycol having the following general formula:



where R'' is a divalent radical having 2 to 4 carbon atoms, and x can adopt a value of from 0 to 50.

Examples of suitable aromatic dicarboxylic acids are terephthalic acid, isophthalic acid, 1,4-, 1,5-, 2,6- and 2,7-naphthalenedicarboxylic acid, diphenic acid and 4,4'-oxybis (benzoic acid). Up to 30 mol % of these dicarboxylic acids may be replaced by aliphatic or cycloaliphatic dicarboxylic acids, for example succinic acid, adipic acid, sebacic acid, dodecanedioic acid or cyclohexane-1,4-dicarboxylic acid.

Examples of suitable polyesters are polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polyethylene 2,6-naphthalate, polypropylene 2,6-naphthalate and polybutylene 2,6-naphthalate.

The preparation of these polyesters is known (DE-A 24 07 155 and 24 07 156; Ullmanns Encyclopadie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry], 4th Ed., Vol. 19, pages 65 ff., Verlag Chemie, Weinheim, 1980).

The polyester molding composition may comprise any one of these polyesters or a plurality of polyesters in the form of a mixture. Furthermore, up to 40% by weight of other thermoplastics may be present so long as they do not adversely affect the bonding ability, in particular impact-modifying rubbers, as already indicated above for the polyamide. Furthermore, the polyester molding composition may comprise the conventional auxiliaries and additives for polyesters, such as, for example, flame retardants, stabilizers, processing auxiliaries, fillers, in particular for improving the electrical conductivity, reinforcing fibers, pigments or the like. The amount of said agents should be metered in such a way that the desired properties are not seriously impaired.

In general, the polyamide molding composition has a continuous polyamide phase and the polyester molding composition has a continuous polyester phase.

If the composite contains a layer of a polyamide molding composition, the adhesion promoter, in a preferred embodiment, comprises a polyamide in addition to the graft copolymer, particularly preferably in an amount of from 10 to 90% by weight, including 20, 30, 40, 50, 60, 70, and 80% by weight, inclusive of all values and subranges therebetween, based on the sum of graft copolymer and polyamide.

If the composite contains a layer of a polyester molding composition, the adhesion promoter, in a further preferred embodiment, comprises a polyester in addition to the graft copolymer, particularly preferably from 10 to 90% by weight, including 20, 30, 40, 50, 60, 70, and 80% by weight, inclusive of all values and subranges therebetween, based on the sum of graft copolymer and polyester.

If the composite contains a layer I of a polyamide molding composition and a layer II of a polyester molding compo-

sition which are bonded to one another by the adhesion promoter according to the invention, it is preferred that the adhesion promoter comprises both a polyamide and a polyester in addition to the graft copolymer. Corresponding molding compositions are likewise a subject matter of the invention.

In this embodiment, the adhesion promoter preferably comprises the following composition:

I. from 5 to 60 parts by weight of a graft copolymer prepared using the following monomers:

a) from 0.5 to 25% by weight, based on the graft polymer, of a polyamine having at least 4, preferably at least 8 and particularly preferably at least 11 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, preferably of at least 500 g/mol and particularly preferably of at least 800 g/mol, and

b) polyamide-forming monomers selected from lactams, α -aminocarboxylic acids and/or equimolar combinations of diamine and dicarboxylic acid;

II. from 10 to 85 parts by weight of a polyamide;

III. from 10 to 85 parts by weight of a polyester; where the sum of the parts by weight of I, II and III is 100; and
IV. a maximum of 40 parts by weight of additives selected from impact-modifying rubber and/or conventional auxiliaries or added materials.

The polyamide component II of the adhesion promoter should be readily compatible with the polyamide of layer I and thus should additionally facilitate good adhesion. Suitable polyamide combinations are known to the person skilled in the art or can easily be determined by simple routine experiments, for example by means of pressed plates. It is frequently sufficient for the two polyamides to have at least one monomer unit in common or for the two to have a monomer unit corresponding to one another with the same number of carbon atoms or with the same length. Ideally, the polyamide should substantially correspond to the polyamide of layer I.

The same applies to the polyester component III of the adhesion promoter, which should be readily compatible with the polyester of layer II. Here too, suitable polyester combinations are known to the person skilled in the art or can easily be determined by simple routine experiments, for example by means of pressed plates. It is frequently sufficient for the two polyesters to have at least one monomer unit in common or for corresponding monomer units to be at least similar. Ideally, the polyester should substantially correspond to the polyester of layer II.

Besides the graft copolymer and, where appropriate, the polyamide and/or the polyester, the adhesion promoter can also comprise further components as additives, such as, for example, an impact-modifying rubber and/or auxiliaries or added materials, as explained in greater detail above as possible constituents of layers I and II. The amount of all additives is, in total, a maximum of 40 parts by weight, preferably a maximum of 30 parts by weight and particularly preferably a maximum of 20 parts by weight.

The multilayer composite according to the invention is, in one embodiment, a pipe, a filler neck or a tank, in particular for the transport or storage of liquids or gases. A pipe of this type can have a straight or corrugated shape or may only be corrugated in sections. Corrugated pipes are known, for example those described in U.S. Pat. No. 5,460,771. Important applications for the multilayer composites according to the present invention are fuel lines, tank filler necks, vapor lines (i.e. lines in which fuel vapors are transported, for example vent lines), gasoline pump hoses and piping, cooling fluid lines, air-conditioning unit lines or fuel tanks.

The multilayer composite according to the invention can also be in the form of a flat composite, for example as a film, such as a packaging film for foods, as a composite element with a top layer having improved UV resistance, or as an extruded multilayer plate.

When the multilayer composite according to the invention is used for transporting or storing flammable liquids, gases or dusts, such as, for example, fuel or fuel vapors, it is advisable to provide one of the layers belonging to the composite or an additional inner layer with an electrically conductive finish. This can be carried out by compounding one or more of the layers with an electrically conductive additive by conventional methods. Examples of conductive additives which can be used are conductive carbon black, metal flakes, metal powder, metallized glass beads, metallized glass fibers, metal fibers (for example made from stainless steel), metallized whiskers, carbon fibers (also metallized), intrinsically conductive polymers or graphite fibrils. It is also possible to employ mixtures of different conductive additives. In the preferred case, the electrically conductive layer is in direct contact with the medium to be transported or stored and has a maximum surface resistance of $10^9 \Omega$ per square.

When the multilayer composite according to the invention is a pipe, it can also be sheathed with an additional elastomer layer. Both cross-linking rubber compositions and thermoplastic elastomers are suitable for the sheathing. The sheathing can be applied to the pipe either with or without an additional adhesion promoter, for example by means of extrusion via a crosshead die or by pushing a prefabricated elastomer tube over the already-extruded multilayer pipe.

The multilayer composite can be manufactured in one or more steps. For example one-step processes may include conventional multi-component injection molding methods, coextrusion methods or coextrusion blow molding methods. Multi-step processes, may include, for example, those described in U.S. Pat. No. 5,554,425.

The multilayer composite can consist, in the simplest embodiment, of the layer I, the adhesion promoter and the layer II. If additional layers are used, however, the following layer configurations, for example, may also be provided:

- rubber/layer I/adhesion promoter/layer II;
- layer I/adhesion promoter/layer II/electrically conductive layer II;
- layer I/adhesion promoter/layer II/adhesion promoter/layer I;
- layer I/adhesion promoter/layer II/adhesion promoter/electrically conductive layer I;
- rubber/layer I/adhesion promoter/layer II/adhesion promoter/layer I/electrically conductive layer I;
- and layer II/adhesion promoter/layer I/electrically conductive layer I.

The results given in the examples were determined with the aid of the following measurement methods.

In order to determine the concentration of carboxyl end groups in the graft copolymer, 1 g of graft copolymer was dissolved in 50 ml of benzyl alcohol at 165° C. under a nitrogen blanket. The graft copolymer was dissolved for a maximum of 20 minutes. The solution was titrated with a solution of KOH in ethylene glycol (0.05 mol of KOH/l) using a phenolphthalein indicator, until the color change occurred.

In order to determine the concentration of amino groups in the graft copolymer, 1 g of the graft copolymer was dissolved in 50 ml of m-cresol at 25° C. The solution was titrated potentiometrically with perchloric acid.

The determination of the solution viscosity η_{rel} (relative viscosity) was carried out using a 0.5% by weight solution of the graft copolymer in m-cresol at 25° C. in accordance with DIN 53727/ISO 307.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only, and are not intended to be limiting unless otherwise specified.

EXAMPLES

The following components were used in the experiments: Graft copolymer 1:

29.7 kg of lauroilactam was melted at from 180° C. to 210° C. in a heating kettle and transferred into a pressure-tight polycondensation reactor; 1.5 kg of water and 1.71 g of hypophosphorous acid were subsequently added. The lauroilactam cleavage was carried out at 280° C. at the inherent pressure generated within the reactor. The pressure within the reactor was then reduced to a residual steam pressure of 3 bar over the course of 3 hours, and 300 g of polyethyleneimine (LUPASOL G 100 from BASF AG, Ludwigshafen) was then metered into the reactor. The polyethyleneimine was reacted with the mixture at the inherent pressure generated within the reactor. The pressure in the reactor was subsequently reduced to atmospheric pressure, and nitrogen was then passed over the melt at 280° C. for 2 hours. The clear melt was discharged as an extrudate via a melt pump, cooled in a water bath and subsequently granulated. The graft copolymer 1 had the following properties:

η_{rel} : 1.68 Melting point T_m : 175° C. Amino group concentration: 225 mmol/kg Carboxyl end group concentration: <10 mmol/kg

Graft copolymer 2:

9.5 kg of lauroilactam was melted at from 180° C. to 210° C. in a heating kettle and transferred into a pressure-tight polycondensation reactor; 475 g of water and 0.54 g of hypophosphorous acid were subsequently added. The lauroilactam cleavage was carried out at 280° C. at the inherent pressure generated inside the reactor. The reactor pressure was then reduced to a residual steam pressure of 5 bar over the course of 3 hours, and 500 g of polyethyleneimine (LUPASOL G 100 from BASF AG, Ludwigshafen) and 15 g of dodecanedioic acid were metered in. The two components were reacted at the inherent pressure generated inside the reactor. The reactor pressure was subsequently reduced to atmospheric pressure, and nitrogen was then passed over the melt at 280° C. for 2 hours. The clear melt was discharged as an extrudate via a melt pump, cooled in a water bath and subsequently granulated. The graft copolymer 2 had the following properties:

η_{rel} : 1.52 Melting point T_m : 169° C. Amino group concentration: 810 mmol/kg Carboxyl end group concentration: <10 mmol/kg

PA 1: extrudable PA12 molding composition having η_{rel} =2.1 and an excess of carboxyl end groups.

PA 2: extrudable PA12 molding composition having η_{rel} =2.1 and an excess of amino end groups.

PES 1: VESTODUR 1000, a homopolybutylene terephthalate from Degussa-Huls AG having a solution viscosity η_{sp}/c measured in phenol/o-dichlorobenzene (1:1), of 107 cm²/g.

PES 2: VESTODUR 3000, a homopolybutylene terephthalate from Degussa-Huls AG having a solution viscosity η_{sp}/c of 165 cm²/g.

EXXELOR VA 1803: an EPM rubber functionalized with about 1% of maleic anhydride, from Exxon Chemical, Cologne

Polyamide of layer I:

PA 3: Extrudable, plasticized, impact-modified PA 12 molding composition having $\eta_{\text{sp}}/\text{c} = 2.1$ and an excess of carboxyl end groups

Polyester of layer II:

PES 3: VESTODUR 2000, a homopolybutylene terephthalate from Degussa-Huls AG having a solution viscosity J of $145 \text{ cm}^3/\text{g}$

Example 1

A pressed-plate three-layer composite was produced from PA 3 (layer I), graft copolymer 1 as adhesion promoter and PES 3 (layer II) at 250°C . and a pressing time of 30 seconds. Inseparable adhesion was obtained here both to the polyester layer and to the polyamide layer.

Example 2

As in Example 1, but with graft copolymer 2 as adhesion promoter. Here too, inseparable adhesion was obtained both to the polyester layer and to the polyamide layer.

Comparative Example 1

As in Example 1, a pressed-plate composite was produced from PA 3 (layer I) and PES 3 (layer II). Instead of the graft copolymer 1, LUPASOL G 100 in anhydrous form was applied in a very thin layer to the upper side of the PA 3 plate which was to be bonded to PES 3. After the pressing and cooling, the plate was removed, and the layer adhesion was tested. It was found that no adhesion was present.

Comparative Example 2

Four different blends of PA 2 and polyethylenimine (LUPASOL G 100 in anhydrous form, from BASF AG, Ludwigshafen) were produced in accordance with Table 1 in a Haake laboratory compounder.

TABLE 1

| Blend component | Blends of polyamide and polyethylenimine | | | |
|------------------|--|----|----|----|
| | Parts by weight | | | |
| PA 2 | 99 | 95 | 90 | 80 |
| Polyethylenimine | 1 | 5 | 10 | 20 |

The mixing was carried out at 180°C . and 64 rpm over the course of 8 minutes.

The mixtures were subsequently comminuted and applied to an injection-molded plate of PES 1 which was in a press mold and subsequently pressed as indicated in Example 1.

In all four cases, it was found on checking the layer adhesion that the composite was poorly bonded, and could be separated at the interface even by hand.

Adhesion Promoter blends:

AP 1 (not according to the invention):

12.6 kg of PA 1 and 22.82 kg of PES 1 were mixed as melts, extruded and granulated in a Berstorff ZE 25 33D twin-screw compounder at 270°C . and 200 rpm and with a throughput of 10 kg/h.

AP 2 (according to the invention):

12.6 kg of PA 2, 22.82 kg of PES 1 and 5.0 kg of graft copolymer 2 were mixed as melts, extruded and granulated in a Berstorff ZE 25 33D twin-screw compounder at 270°C . and 150 rpm and with a throughput of 10 kg/h.

AP 3 (according to the invention):

12.6 kg of PA 2, 22.82 kg of PES 2 and 5.0 kg of graft copolymer 2 were mixed as melts, extruded and granulated

in a Berstorff ZE 25 33D twin-screw compounder at 270°C . and 150 rpm and with a throughput of 10 kg/h.

AP 4 (according to the invention):

As in AP 3, but with additional use of 4.0 kg of EXX-ELOR VA 1803.

Comparative Example 3 and Examples 3 to 5

In order to produce the multilayer composites, a tape coextrusion mold having an exit width of 30 mm was used, with the various layers being brought together in the mold just before the exit of the melt from the mold. The mold was fed by three Storck 25 extruders. After exiting the mold, the three-layer composite was laid onto a chill roll and taken off (chill roll process).

The results are shown in the table below; the adhesion scores indicated therein have the following meanings:

0 no adhesion

1 slight adhesion

2 some adhesion; can be separated with little effort

3 good adhesion; can only be separated with great effort and possibly with the aid of tools

4 cannot be separated

| Example (E) or Comparative Example (C) | Layer I | Adhesion promoter | Layer II | Adhesion | |
|--|---------|-------------------|----------|--------------------------------------|---------------------------------------|
| | | | | Layer I/ adhesion promoter interface | Layer II/ adhesion promoter interface |
| C 3 | PA 3 | AP 1 | PES 1 | 0 | 4 |
| E 3 | PA 3 | AP 2 | PES 1 | 4 | 4 |
| E 4 | PA 3 | AP 3 | PES 3 | 4 | 4 |
| E 5 | PA 3 | AP 4 | PES 1 | 4 | 4 |

Examples 4 and 5 according to the invention were additionally repeated in modified form by producing three-layer pipes with the corresponding layer configuration (with PA 3 as the outer layer). The results are identical: in all cases an adhesion score of 4 was obtained.

In all the cases investigated, the long-term resistance of the multilayer composites in contact with alcohol-containing fuel was excellent both at 40°C . and at 60°C .

The priority document of the present application, German patent application 19929883.1 filed Jun. 29, 1999 and German patent application 10005641.5, filed Feb. 9, 2000, are incorporated herein by reference.

Obviously, numerous modifications and variations on the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and is intended to be secured by Letters Patent is:

1. A thermoplastic multilayer composite which comprises:
I) at least one layer I of a thermoplastic molding composition;

II) at least one layer II of a further thermoplastic molding composition; and at least one layer of an adhesion promoter disposed between at least one layer I and at least one layer II, wherein said adhesion promoter comprises at least 5% by weight of a graft copolymer comprising the following monomers:

a) from 0.5 to 25% by weight, based on the total amount of graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, and

- b) polyamide-forming monomers selected from the group consisting of lactams, ω -aminocarboxylic acids, equimolar mixtures of diamines and dicarboxylic acids, and mixtures thereof.
2. The thermoplastic multilayer composite of claim 1, wherein at least one of layer I or layer II comprises a polyamide molding composition or a polyester molding composition.
3. The thermoplastic multilayer composite of claim 1, wherein layer I comprises a polyamide molding composition and layer II comprises a polyester molding composition.
4. The thermoplastic multilayer composite of claim 1, wherein the polyamine contains at least 8 nitrogen atoms.
5. The thermoplastic multilayer composite of claim 1, wherein the polyamine contains at least 11 nitrogen atoms.
6. The thermoplastic multilayer composite of claim 1, wherein the polyamine has a number average molecular weight M_n of at least 500 g/mol.
7. The thermoplastic multilayer composite of claim 1, wherein the polyamine has a number average molecular weight M_n of at least 800 g/mol.
8. The thermoplastic multilayer composite of claim 1, wherein the graft copolymer has an amino group concentration in the range of from 100 to 2500 mmol/kg.
9. The thermoplastic multilayer composite of claim 1, wherein the graft copolymer further comprises:
- c) an oligocarboxylic acid, selected from the group consisting of a dicarboxylic acid and a tricarboxylic acid.
10. The thermoplastic multilayer composite of claim 9, wherein the amount of dicarboxylic acid is 0.015 to 3 mol %, and the amount of tricarboxylic acid is 0.01 to 1.2 mol % based on the total moles of polyamide-forming monomers.
11. The thermoplastic multilayer composite of claim 1, wherein the adhesion promoter further comprises at least one polymer selected from the group consisting of a polyamide and polyester.
12. The thermoplastic multilayer composite of claim 2, wherein the adhesion promoter further comprises at least one polymer selected from the group consisting of a polyamide and polyester.
13. The thermoplastic multilayer composite of claim 3, wherein the adhesion promoter further comprises at least one polymer selected from the group consisting of a polyamide and polyester.
14. The multilayer composite of claim 1, which comprises one layer I and one layer II.
15. The multilayer composite of claim 1, wherein at least one layer of said multilayer composite has been rendered electrically conductive.
16. A hollow article comprising the multilayer composite of claim 1.
17. The hollow article of claim 16, wherein said hollow article is a pipe.
18. The hollow article of claim 17, which is fully corrugated or partially corrugated.
19. The hollow article of claim 17 having an interior and an exterior surface, wherein the interior surface layer has been rendered electrically conductive.
20. The hollow article of claim 17 having an interior and an exterior surface, wherein the exterior surface layer is comprised of rubber.

21. The hollow article of claim 17, wherein said pipe is a fuel line, a brake fluid line, a cooling fluid line, a hydraulic fluid line, a gas station line, an air conditioning unit line or a vapor line.
22. The hollow article of claim 16, wherein said hollow article is a tank, a fuel tank, a filler neck, or a fuel tank filler neck.
23. A plate comprising the multilayer composite of claim 1.
24. The multilayer composite of claim 1, made by multi-component injection molding, coextrusion or coextrusion blow molding.
25. The hollow article of claim 16, made by multi-component injection molding, coextrusion or coextrusion blow molding.
26. The plate of claim 22, made by multi-component injection molding, coextrusion or coextrusion blow molding.
27. An adhesion promoter comprising at least 5% by weight of a graft copolymer comprising the following monomers:
- a) from 0.5 to 25% by weight, based on the total amount of graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, and
- b) polyamide-forming monomers selected from the group consisting of lactams, ω -aminocarboxylic acids, equimolar mixtures of diamines and dicarboxylic acids, and mixtures thereof.
28. An adhesion promoter comprising:
- I) from 5 to 60 parts by weight of a graft copolymer comprised of the following monomers:
- a) from 0.5 to 25% by weight, based on the total amount graft copolymer, of a polyamine having at least 4 nitrogen atoms and having a number average molecular weight M_n of at least 146 g/mol, and
- b) polyamide-forming monomers selected from the group consisting of lactams, ω -aminocarboxylic acids, equimolar mixtures of diamines and dicarboxylic acids, and mixtures thereof,
- II) from 10 to 85 parts by weight of a polyamide;
- III) from 10 to 85 parts by weight of a polyester; wherein the sum of the parts by weight of I, II, and III is 100;
- IV) a maximum of 40 parts by weight of additives comprising at least one additive selected from the group consisting of impact-modifying rubber, flame retardants, stabilizers, plasticizers, fillers, reinforcing fibers, and processing auxiliaries.
29. A method of adhering at least two layers of a thermoplastic multilayer composite using the adhesion promoter of claim 27.
30. A method of adhering at least one polyamide to at least one polyester using the adhesion promoter of claim 27.
31. A method of adhering at least one polyamide to at least one polyester using the adhesion promoter of claim 28.



United States Patent [19]

Shimura et al.

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[54] **MEDICAL TOOL HAVING LUBRICIOUS SURFACE IN A WETTED STATE AND METHOD FOR PRODUCTION THEREOF**

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4-202441 7/1992 Japan .
WO92/19289 11/1992 WIPO .

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[57] **ABSTRACT**

This invention provides a medical tool the surface of which is enabled to acquire lasting lubricity (low friction) by assuming a state wetted with bodily fluid or aqueous solution. This surface is formed without requiring the coating work to be repeated. The medical tool is produced by coating a water-swellaable polymer having in the molecular unit thereof a reactive functional group capable of being reacted with a proton-donating group, on the surface of a matric material possessing the proton-donating group, and also by coating a water-swellaable polymer having in the molecular unit thereof a reactive group capable of being reacted with an acid anhydride group on the surface of a matric material possessing the acid anhydride group.

18 Claims, 1 Drawing Sheet

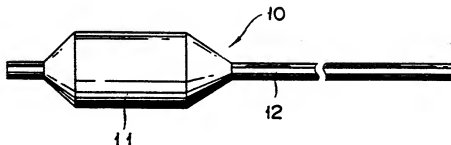


FIG. 1

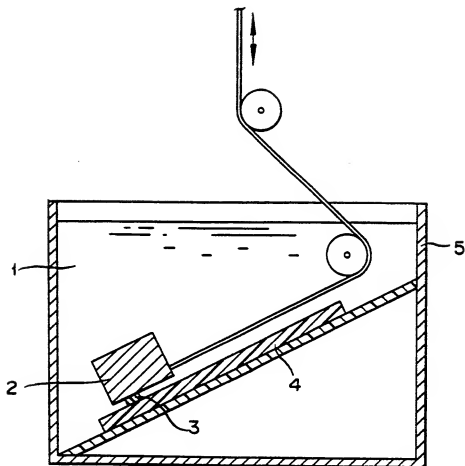
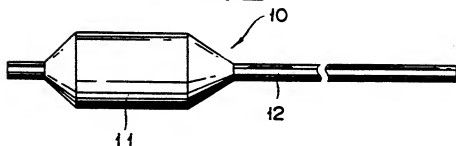


FIG. 2



MEDICAL TOOL HAVING LUBRICIOUS SURFACE IN A WETTED STATE AND METHOD FOR PRODUCTION THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a medical tool and a method for the production thereof. More particularly, it relates to a medical tool which, owing to a polymer deposited on the surface thereof, manifests excellent lubricity on being wetted and a method for the production of the medical tool.

1. Description of the Prior Art

Generally, for the manufacture of catheters and other similar medical tools, substances of low friction are adopted as matric materials thereof and further such matric materials are coated with a hydrophilic polymer for the sake of precluding the medical tools from inflicting damage on the inner wall surfaces of blood vessels or on the tissues and enhancing the operability of the medical tools. For example, fluorine resin, polyethylene resin, etc. are used as substances of low friction for matric materials and these matric materials are coated with fluorine resin, silicone oil, olive oil, glycerol, etc.

These measures, however, cannot be expected to impart lasting lubricity to the medical tools. The medical tools which embody these measures have a problem of poor safety in the sense that the lubricious substances are liable to exfoliate, peel, or melt from the surfaces of the medical tools.

U.S. Pat. No. 4,100,309 makes a disclosure to the effect that a copolymer of polyvinyl pyrrolidone with polyurethane is used as a substance possessed of lubricity. The method taught by this US patent publication is satisfactory in terms of lubricity and lastingness of this quality. Since this method requires at least two kinds of polymer for coating and essentially necessitates the presence of an isocyanate group as a reactive group on the surface of the matric material, the reaction is not obtainable with either a matric material allowing no easy introduction of the isocyanate group or a polymer possessed of lubricity.

JP-A-59-81,341 also discloses a method for impartation of lubricity similarly by utilizing an isocyanate group on the surface of a matric material.

Further, JP-B-1-55,023 discloses a method for binding a copolymer of polyether, polyamide, or polysiloxane through the medium of polyisocyanate to the surface of a matric material of a medical tool. For this method, the interposition of the isocyanate is an essential requirement and the presence on the surface of the matric material of at least one group selected from among amino group, imino group, carboxyl group, and mercapto group is an indispensable requirement. This method, therefore, is incapable of effecting this binding treatment on a medical tool which is made of polyolefin or halogenated polyolefin and has none of the functional groups mentioned above.

The various methods of surface lubrication mentioned above, however, are not desirable from the standpoint of operability because they require the coating operation to be performed at least twice (as for the coating with a cross-linking compound such as isocyanate and the coating with a lubricious substance) when lasting lubricity must be imparted.

Generally, since a low molecular cross-linking agent (such as, for example, a diisocyanate compound or a

diepoxy compound which has a highly active functional groups) is possessed of unduly high reactivity, remains as unreacted monomer which is easy to elute and has toxicity, the use of such a substance is not desirable even from the standpoint of safety.

As described above, the impartation of lubricity to the surface of a medical tool imposes a limit on the kind of matric material or requires the coating operation to be carried out twice or more where lasting lubricity is necessary.

An object of this invention, therefore, is to provide a novel medical tool and a method for the production thereof.

Another object of this invention is to provide a medical tool the surface of which acquires lasting lubricity (low friction) on being wetted with body fluid or aqueous solvent, obviates the necessity of carrying out the coating operation twice or more for its own formation, and enjoys high safety and a method for the production of the medical tool.

SUMMARY OF THE INVENTION

The objects described above are accomplished by a medical tool which comprises a water-swellaible polymer containing a reactive functional group in the molecular unit thereof and a matric material capable of reacting with the reactive functional group and manifests lubricity on being wetted.

This invention discloses a medical tool wherein the matric material contains a proton-donating group which is capable of reacting with the reactive functional group. The invention also discloses a medical tool wherein the reactive functional group is at least one group selected from the class consisting of epoxy group, acid halide group, and isocyanate group. This invention further discloses a medical tool wherein the proton-donating group is at least one group selected from the class consisting of amino group, imino group, hydroxyl group, carboxyl group, and mercapto group. Further, this invention discloses a medical tool wherein the matric material is a material having as one component thereof a synthetic polymeric compound containing an acid anhydride group in the molecular unit thereof and the reactive functional group is capable of reacting the acid anhydride group.

The objects described above are also accomplished by a method for the production of a medical tool manifesting lubricity on being wetted, which method comprises coating the surface of a matric material having as a component thereof a synthetic polymeric compound containing an acid anhydride group in the molecular unit thereof with a water-swellaible polymer possessed of a functional group capable of reacting with the acid anhydride group and subsequently heat-treating the coated matric material at a temperature of not lower than 40° C.

The objects described above are further accomplished by a method for the production of a medical tool manifesting lubricity on being wetted, which method comprises coating the surface of a matric material having as a component thereof a synthetic polymeric compound containing an acid anhydride group in the molecular unit thereof with a water-swellaible polymer possessed of a functional group capable of reacting with the acid anhydride group and subsequently cross-linking the water-swellaible polymer.

This invention discloses a medical tool forming a lubricious surface on being wetted, wherein a water-swellaible polymer containing in the molecular unit thereof at least one reactive functional group selected from among epoxy group, acid halide group, and isocyanate group is applied in the form of a coating to the surface of a matric material containing a proton-donating group such as amino group, imino group, hydroxyl group, carboxyl group, or mercapto group which is capable of reacting with the reactive functional group mentioned above. This invention also discloses a medical tool, wherein a water-swellaible polymer containing in the molecular unit thereof at least one reactive functional group such as hydroxyl group, amino group, or epoxy group which is capable of reacting with an acid anhydride is applied in the form of a coating to the surface of a matric material containing an acid anhydride group in the molecular unit thereof. This invention further discloses a medical tool, wherein a water-swellaible polymer is introduced fast chemically in the surface of the matric material. For the reason above, the medical tool of this invention can retain high safety intact because it never entails such phenomenon of an applied coat exfoliating, peeling, or melting from the surface of a matric material as is observed in the case of a method which involves application of silicone oil, olive oil, or glycerol to the surface of a matric material.

Further, in the medical tool of this invention, the surface of the matric material thereof offers extremely low friction resistance particularly when it is in a state wet with such bodily humor as saliva, digestive fluid, or blood or such aqueous liquid as physiological saline solution or water. When the catheter, i.e. one form of the medical tool of this invention, is inserted in a patient's body, therefore, it is at an advantage in facilitating the insertion, alleviating the patient's pain, and precluding infliction of injury to the mucous membrane or the inner wall surface of blood vessel, for example.

Besides, since this invention does not need to use such a highly reactive cross-linking compound as diisocyanate for the sake of the coating work but permits impartation of ample prospective lubricity on the surface of the matric material by just one coating work, the medical tool of this invention excels in operability and safety and imposes virtually no restriction on the matric material. Thus, this invention can be embodied in a promiscuous collection of medical tools.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating a method of testing for lubricity and

FIG. 2 is a schematic diagram illustrating a catheter in one preferred embodiment of the medical tool of this invention.

EXPLANATION OF THE PREFERRED EMBODIMENT

In this invention, the water-swellaible polymer which manifests lubricity in a wet state is only required to be capable of manifesting this lubricity on contact with body fluid or aqueous solvent. With respect to the ease with which the polymer is synthesized and the convenience with which the polymer is worked, acrylamide, acrylamide derivatives such as dimethyl acrylamide, maleic anhydride, vinyl methyl ether, etc. may be cited as preferable polymers which answer the description given above. The polymer under discussion is preferable to use dimethyl acrylamide as a main component

thereof. A copolymer (I) which comprises a moiety destined to manifest lubricity and a moiety incorporating the aforementioned reactive functional group therein proves particularly preferable. The moiety manifesting lubricity is required to account for a proportion of not less than 40 parts by weight, preferably not less than 60 parts by weight, and more preferably not less than 80 parts by weight, in the total amount of the water-swellaible polymer. The moiety incorporating the reactive functional group is required to account for a proportion of not less than 1 part by weight, preferably not less than 10 parts by weight, and more preferably not less than 20 parts by weight. Produced by synthesis, the polymer capable of manifesting lubricity on contact with liquid may be chemically treated to be partially substituted by an epoxy group, an acid halide group, an isocyanate group, etc.

Further, the matric material of the medical tool aimed at by this invention may be a shaped article formed chiefly of such a material as modified polyolefin, polyether, polyurethane, polyamide, polyimide, or nylon, which is a substance containing a functional group capable of reacting with the epoxy group, acid halide group, isocyanate group, etc., namely a proton-donating group such as amino group, imino group, hydroxyl group, carboxyl group, or mercapto group or a multilayer shaped article using other material in addition to the material mentioned above or a shaped article of an alloy based on the same material as mentioned above. In the light of the convenience of handling, it is preferable to use a polyolefin modified with acrylic acid for the matric material. At least part of the surface of the matric material of the medical tool, when necessary, may be treated as by the method of plasma-initiated graft polymerization so as to introduce a proton-donating group therein. The content of the material in the medical tool, though variable with the mechanical strength and other qualities to be preferable, is at least 50 parts by weight, preferably at least 70 parts by weight, and more preferably at least 90 parts by weight.

The term "acid anhydride" refers to a compound which is formed by the condensation of two molecules of carboxylic acid with loss of one molecule of water and is represented by the general formula, $(RCO)_2O$. Though the synthetic polymeric compound which contains an acid anhydride group in the molecular unit thereof is not particularly limited, monomers containing an acid anhydride group such as, for example, polymeric compounds synthetically formed by copolymerizing maleic anhydride may be cited as preferred examples. Polyethylenes and polypropylenes which contain maleic anhydride are particularly preferable examples. The demand for the polyolefins containing maleic anhydride as an adhesive polymer fit for the modification of an olefin or the lamination of a multilayer olefin product has been growing in recent years. They are produced and marketed under a general designation of "Modified Polyolefins" and, therefore, are readily available. They are thermoplastic polymers excelling in formability and prove preferable in terms of physical properties, workability, stability (resistance to aging), safety, and cost.

The synthetic polymeric compound containing an acid anhydride has only to be present in the surface layer of the matric material. The matric material, therefore, may be what is manufactured by forming the polymeric compound as a simple substance in a prescribed shape or what is manufactured by having an alloy of the polymeric compound deposited on the surface of a

matrix material formed preparatorily in the prescribed shape. For example, a layer of the synthetic polymeric compound containing an acid anhydride group may be deposited by the multilayer molding, laminating, coating, or blending technique only on such a portion of the surface of a matrix material of polyolefin, polyether, polyurethane, polyamide, polyimide, polyester, or copolymer thereof as is required to offer low friction.

The content of the acid anhydride group is preferable to exceed 0.01 mol %, preferably to fall in the range of 0.5 to 50 mol %, based on the amount of the molar composition of the monomer forming the synthetic polymeric compound plus the acid anhydride group. The functional groups which effectively react with the acid anhydride group include hydroxy group, amino group, and epoxy group, for example. From the viewpoint of reactivity, the epoxy group proves preferable among other functional groups mentioned above. The water-swellaible polymer containing such a functional group is a polymeric compound which is dissolved or swelled with water. As typical examples of the water-swellaible polymer, copolymers (II) of such hydrophilic monomers as acryl amides including acryl amide and dimethyl acrylamide, vinyl pyrrolidone, and vinyl ethers with monomers containing such a functional group as mentioned above may be cited. In the water-swellaible polymer, the content of the functional group capable of reacting with the acid anhydride group is preferable to be in the range of 2 to 50%, preferably 5 to 25%, based on the molar composition of the hydrophilic monomer and the acid anhydride group.

As a method for binding the copolymer (II) to the surface of the matrix material, a heat treatment to be carried out at a temperature exceeding 30° C. is available. The heat treatment promotes the reaction of the water-swellaible polymer with the acid anhydride on the surface of the matrix material and the reaction of the water-swellaible polymer. The temperature of this heat treatment is preferable to be in the range of 30° to 120° C., preferably 50° to 80° C. For the purpose of promoting the reaction of the acid anhydride, a catalyst, particularly the catalyst using such a tertiary amine compound as a trialkyl amine compound or pyridine, is used advantageously. Then, for the purpose of improving the durability or controlling the lubricity of the hydrophilic low-friction surface, the water-swellaible polymer may be coated and then subjected to a cross-linking treatment. To be specific, the strength of the lubricious surface layer can be exalted without appreciably decreasing the lubricity thereof by allowing a three-dimensional reticular structure to be formed in a small amount within the surface layer. If the cross-linked structure is unduly large, however, the ability of the surface layer to swell with absorbed liquid is lowered and the ability of the surface to resist friction is impaired. Thus, the formation of a cross-link in the surface layer calls for due advertence. The cross-linkage may be attained by any of the various conventional methods widely known in the art. The polymer may be cross-linked, for example, by generating an active radical by means of light, heat, or radiation. Besides, a method which involves addition of a polymerizing polyfunctional monomer, a method which involves application of a polyfunctional cross-linking agent, and a method which resorts to cross-linkage of functional groups in the molecular unit through the medium of a catalyst may be cited as typical examples of the conventional methods mentioned above. In the case of a water-swellaible polymer con-

taining such a highly reactive functional group as an epoxy group, for example, the polymer between epoxy groups can be easily cross-linked with a diamino compound, dihydroxy compound, dialdehyde compound, etc.

The copolymers (I) or copolymers (II) may occur as random, block, and graft copolymers. The block or graft copolymers prove preferable. The preference of the block copolymers and the graft copolymers over the random copolymers will be demonstrated below with reference to copolymers of vinyl pyrrolidone (VP) and glycidyl methacrylate (GMA). The block copolymers and the graft copolymers severally of VP and GMA possess a domain manifesting reactivity (poly GMA) and exhibit strong reactivity and bonding property with the acid anhydride group on the surface of the matrix material as compared with polymers which have reactive groups (GMA) and hydrophilic groups (VP) randomly dispersed therein. This fact may be logically explained by a postulate that the poly GMA part is hydrophobic as compared with the poly VP part and excels the poly VP part in adhesiveness to the surface of the matrix material and, therefore, gains in reactivity with the acid anhydride group in the surface layer of the matrix material. As respects the union (cross-linkage) of molecules through the medium of the poly GMA domain, the surface layer is so modified as to acquire increased strength because a plurality of bonds (cross-links) are formed after the pattern of a chain. The randomly introduced GMA, by contrast, possesses less reactivity with the acid anhydride on the surface of the matrix material owing to the influence of the VP which exists in proximity of the GMA molecules. Further, the poly DMAA domains such as are contained in the block copolymers have an ample capacity for absorbing water and, therefore, are enabled to manifest ideal lubricity. The copolymers which have GMA randomly dispersed therein suffer from poor lubricity because the ability of DMAA to absorb water or swell with water is restrained by the intramolecular cross-linkage randomly formed between GMA's and the hydrophobicity of the GMA itself.

The term "medical tool" as used in this invention refers to a medical tool which has formed on either the inner side or the outer side thereof a surface required to offer low resistance to friction during the insertion, slide, or retention of the medical tool in a patient's body when the surface is wetted with such a bodily fluid as saliva, digestive fluid, or blood or an aqueous liquid such as physiological saline solution or water. Thus, the following items may be cited as typical examples of the medical tool of this invention.

- 1) Catheters such as stomach catheter, feeding tube, and ED tube which are inserted via the mouth or nose into the stomach and at times left indwelling therein.
- 2) Tubes or cuffs of oxygen catheters, oxygen cannulas, and windpipes, tubes and cuffs of tracheotomy tubes, and catheters such as intratracheal aspiration catheters which are inserted via the mouth or nose into the windpipe and at times left indwelling therein.
- 3) Catheters such as catheters and balloons in urethral catheters, urinal catheters, and balloon catheters which are inserted into the urethra or the renal duct and at times left indwelling therein.
- 4) Catheters such as suction catheters, fluid discharge catheters, and rectal catheters which are inserted into various body cavities or tissues and at times left indwelling therein.

5) Catheters such as indwelling needles, IVH catheters, thermomodulation catheters, angiographic catheters, vasodilating catheters, dilators, or introducers which are inserted into or left indwelling in the blood vessel and guide wires and stylets for such catheters.

6) Endoscopes, contact lenses, etc. for insertion into various internal organs.

Now, this invention will be described more specifically below with reference to working examples of the invention.

EXAMPLES 1 to 3

(A) Production of block copolymer

To 72.3 g of adipic acid dichloride, 29.7 g of triethyl-glycol was added dropwise at 50° C. The resultant mixture was subjected to reduced-pressure distillation at 50° C. for 3 hours to expel the consequently separated hydrochloric acid and obtain 22.5 g of oligoester. The oligoester in this amount and 4.5 g of methyl ethyl ketone added thereto were together added dropwise into a solution comprising 5 g of sodium hydroxide, 6.93 g of 31% hydrogen peroxide, 0.44 g of a surfactant of dioctyl phosphate, and 120 g of water and left reacting therein at -5° C. for 20 minutes. The product consequently obtained was washed with water, washed repeatedly with methanol, and then dried to obtain a polyperoxide (PPO) containing a plurality of peroxide groups in the molecular unit thereof. With 0.5 g of this PPO as a polymerization initiator, 9.5 g of glycidyl methacrylate (GMA) placed in 30 g of benzene as a solvent was stirred at 65° C. for 24 hours under a reduced pressure to be polymerized. The reaction product was reprecipitated in diethyl ether to obtain polyglycidyl methacrylate (PGMA) containing a peroxide group in the PGMA molecular unit. Then, 1.0 g of the PGMA, 9.0 g of dimethyl acryl amide, and 90 g of dimethyl sulfoxide as a solvent were combined, sealed in a reaction vessel under a reduced pressure, and heated at 80° C. for 18 hours to polymerize the monomer. The resultant reaction solution was poured into 2 liters of rapidly stirred diethyl ether to effect separation of a precipitate. The precipitate was isolated by filtration. The separated precipitate was repeatedly refined with tetrahydrofuran (THF) as a good solvent and diethyl ether as a poor solvent and then subjected to reduced-pressure distillation to obtain a block copolymer.

The procedure described thus far was repeated excepting methacrylic acid chloride was used in Example 2 and methacryloyl-oxyethyl isocyanate was used in Example 3 respectively instead of the GMA mentioned above.

(B) Method of test for lubricity

A modified polyolefin (polyethylene modified with methacrylic acid) sheet (produced by Mitsui-DuPont K.K. and marketed under trademark designation of "Nuclei N-1525") was kept immersed in a THF solution containing the aforementioned block polymer in a concentration of 2% by weight at normal room temperature for 30 seconds and then heat-treated for reaction in an oven at 80° C. for 18 hours. Consequently, a lubricious sheet material was obtained.

In a body of water 1 held in a water tank 5, a cylindrical iron weight 2 having a weight of 1 kg was gently mounted on a sheet 4 attached fast to a plastic plate 6 inclined at an angle of 30° with the aid of the lubricious sheet 3 as illustrated in FIG. 1. The weight 2 was slid repeatedly 100 times at a speed of 100 mm/min. on the

sheet 4 over a width of 1 cm to determine the value of resistance to the friction due to the slide.

The value of resistance to the final friction after the 100th slide of the weight on the inclined sheet as the index of lubricity and the change in the value of resistance to friction (Δ value of resistance to friction) of the following formula (1) as the index of continuous lubricity are shown in Table 1.

$$\Delta \text{ Value of resistance to friction} = (\text{Value of resistance to final friction}) - (\text{Value of resistance to initial friction}) \quad (1)$$

Control 1

The same sheets as obtained in Examples 1 to 3 in their uncoated state were tested for lubricity in the same manner as in Example 1. The results are shown in Table 1.

EXAMPLES 4 to 6

(A) Production of random copolymer

A reaction vessel sealable by fusion was charged with 1.0 g of a varying compound (monomer) indicated in Table 1, 9.0 g of dimethyl acryl amide, 0.05 g of azo-bis-isobutyronitrile as an initiator, and 90 g of dimethyl sulfoxide, sealed by fusion under a reduced pressure, and then heated to 80° C. for 18 hours to induce polymerization of the monomers. The reaction solutions were refined in the same manner as in Examples 1 to 3.

(B) Method of test for lubricity

The surface of a polypropylene sheet (produced by Futamura Kagaku K.K. and marketed under product code of "FOP #60") was irradiated for 10 seconds with a low-temperature plasma (A.r: 0.1 Torr) and supplied with methacrylic acid monomer in the gas phase and simultaneously heated at a temperature of 288 K. to graft the surface. The sheet was washed for one day with a good solvent for polymethacrylic acid and then dried. The dry sheet was kept immersed in a THF solution containing the random copolymer in a concentration of 2% by weight at normal room temperature for 30 seconds and then heat-treated to induce a reaction in an oven at 80° C. for 18 hours. Consequently, a lubricious sheet was obtained. The test for lubricity was carried out in the same manner as in Examples 1 to 3. The results are shown in Table 1.

Control 2

The same sheets as treated in Examples 4 to 6 in their uncoated state were tested for lubricity. The results are shown in Table 1.

EXAMPLE 7

(A) Production of random copolymer

A reaction vessel sealable by fusion was charged with 2.0 g of glycidyl acrylate, 8.0 g of maleic anhydride, 0.05 g of azo-bis-isobutyronitrile as an initiator, and 90 g of dimethyl sulfoxide as a solvent, sealed by fusion under a reduced pressure, and then heated at 80° C. for 18 hours to polymerize the monomers. The produced copolymer was refined in the same manner as in Examples 1 to 3.

(B) Method of test for lubricity

A polyurethane sheet (produced by Dow Chemical Company and marketed under trademark designation of "Pellethane") was kept immersed in a THF solution containing the random polymer at a concentration of 2% by weight at normal room temperature for 30 seconds and then heated to induce a reaction in an oven at

80° C. for 18 hours. Then, the maleic anhydride portion of the polymer deposited fast on the sheet was heated in ethanol with sulfuric acid as a catalyst at 60° C. for 6 hours to open the ring and form a half ester of ethanol. Finally, this sheet was given an alkali washing in an aqueous 0.1% by weight of sodium chloride solution containing NaHCO_3 at a concentration of 0.01% by weight at 60° C. for 18 hours. Consequently, a lubricious sheet was obtained. The sheet was tested for lubricity in the same manner as in Examples 1 to 3. The results are shown in Table 1.

Control 3

The same sheet as produced in Example 7 in its uncoated state was tested for lubricity. The results are shown in Table 1.

(B) Method of test for lubricity

The surface of a balloon 11 (3 mm in outside diameter and 45 mm in length) of polyethylene terephthalate illustrated in FIG. 2 was irradiated with a low-temperature plasma (Ar: 0.1 Torr) for 10 seconds and then supplied with methacrylic acid monomer in the gaseous phase and simultaneously heated at a temperature of 288 K. to graft the surface. The balloon 11 was washed with good solvent for polymethacrylic acid for one day and dried. The dried balloon 11 was treated in the same manner as in Example 8 to obtain a lubricious balloon 11. The balloon 11 was connected to a tube 12 (1 mm in outside diameter) to form a catheter 10. This catheter 10 was tested for lubricity by touch of a finger. The results are shown in Table 1.

TABLE 1

| Sample No. | Matrix material | Copolymer | | Value of resistance to final friction | Δ value of resistance to friction |
|------------|---------------------|----------------------------------|---------------------|---------------------------------------|--|
| | | Monomer 1 | Monomer 2 | | |
| Example 1 | Modified polyolefin | Glycidyl methacrylate | Dimethyl acrylamide | 62 gf | 0 |
| Example 2 | Modified polyolefin | Methacrylic acid chloride | Dimethyl acrylamide | 67 gf | 0 |
| Example 3 | Modified polyolefin | Methacryloyloxy ethyl isocyanate | Dimethyl acrylamide | 64 gf | 0 |
| Example 4 | PP-g-MAA | Glycidyl methacrylate | Dimethyl acrylamide | 77 gf | 0 |
| Example 5 | " | Methacrylic acid chloride | Dimethyl acrylamide | 73 gf | 0 |
| Example 6 | " | Methacryloyloxy ethyl isocyanate | Dimethyl acrylamide | 72 gf | 0 |
| Example 7 | Polyurethane | Glycidyl acrylate | Maleic anhydride | 87 gf | 0 |
| Example 8 | PET-g-MAA | Glycidyl acrylate | Maleic anhydride | 83 gf | 0 |
| Example 9 | " | Glycidyl acrylate | Maleic anhydride | Excellent | Excellent |
| Control 1 | Modified polyolefin | — | — | 431 gf | 234 gf |
| Control 2 | PP-g-MAA | — | — | 386 gf | 82 gf |
| Control 3 | Polyurethane | — | — | 412 gf | 186 gf |
| Control 4 | PET-g-MAA | — | — | 377 gf | 84 gf |

EXAMPLE 8

(A) Production of random copolymer

The procedure of Example 7 was faithfully repeated for polymerization and refinement.

(B) Method of test for lubricity

The surface of a polyethylene terephthalate sheet (produced by Dia Foil K.K. and marketed under product code of "H100") was irradiated with a low-temperature plasma (Ar: 0.1 Torr) for 10 seconds and then supplied with methacrylic acid monomer in the gaseous phase and simultaneously heated at a temperature of 288 K. to be grafted. The sheet was washed with a good solvent for polymethacrylic acid for one day and dried. The dried sheet was treated in the same manner as in Example 7 to obtain a lubricious sheet. The test for lubricity was carried out in the same manner as in Examples 1 to 3. The results are shown in Table 1.

Control 4

The same sheet as produced in Example 8 in its uncoated state was tested for lubricity. The results are shown in Table 1.

EXAMPLE 9

(A) Production of random copolymer

The procedure of Example 8 was faithfully repeated for both polymerization and refinement. The results are shown in Table 1.

Note)

(PP-g-MAA: Graft polymerization of methacrylic acid monomer to polypropylene

PET-g-MAA: Graft polymerization of methacrylic acid monomer to polyethylene terephthalate

EXAMPLES 10 and 11

A block copolymer of Example 10 was obtained by polymerizing 3.0 g of polyglycidyl methacrylate and 12.5 g of dimethyl acrylamide by following the procedure described in (A) production of block copolymer in Example 1.

A random copolymer of Example 11 was obtained by polymerizing 3.0 g of glycidyl methacrylate and 12.5 g of dimethyl acrylamide by following the procedure described in (A) production of random copolymer in Example 4.

Tetrahydrofuran solutions severally containing the block copolymer and the random copolymer mentioned above at a fixed concentration of 2% by weight were tested for lubricity in the same manner as in Examples 1 to 3, but slide time was 500. The results are shown in Table 2.

TABLE 2

| Kind of polymer | DMAA : GMA (found by NMR) | Value of resistance (gf) | |
|-----------------------------------|------------------------------|-----------------------------|----------------|
| | | Initial | Δ value |
| Block copolymer of Example 10 | 7.81 : 1 | 89.2 | 2.6 |
| Random copolymer of Example 11 | 7.78 : 1 | 75.8 | 37.5 |

EXAMPLES 12 to 14

A block copolymer (Example 12) having poly GMA as a reactive domain and poly DMAA as a hydrophilic domain was obtained by placing 8 g of dimethyl acrylamide (DMAA) as a hydrophilic monomer in DMSO using 1 g of the poly GMA of Example 1 as a polymerization initiator and polymerizing the monomers at 70° C. for 18 hours. On analysis by NMR, the resultant copolymer was found to be composed of DMAA and GMA at a ratio of 10:1.1. In the same manner as described above, a block copolymer composed of DMAA and GMA at a ratio of 7.1:1 was obtained in Example 13 and a block copolymer composed of vinyl pyrrolidone and GMA at a ratio of 6.6:1 in Example 14.

A sheet (200 μ m) of an ethylene-acrylic ester-maleic anhydride terpolymer (produced by Sumika-CDF Kagaku K.K. and marketed under trademark designation of "Bondine TX8030") was kept immersed in a tetrahydrofuran (THF) solution (containing 1% by weight of pyridine) containing the block copolymer at a concentration of 2% at 25° C. for 30 seconds, heat-treated for reaction in an oven at 80° C. for 18 hours, washed with water, and dried. The produced sheet, on exposure to moisture, assumed a ropy lubricious surface offering only low resistance to friction.

When the block copolymers were tested for lubricity with an apparatus shown in FIG. 1 in the same manner as in Examples 1 to 8, the values of resistance to friction were in the neighborhood of 70 gf and the values of Δ resistance to friction were invariably below 10 gf. In the test of 100 slides on the plate, they showed low friction resistance stably. When the obverse surface and the cross section of each of the sheets were visually examined under a scanning type electron microscope (produced by Japan Electron Optics Laboratory Co., Ltd. and marketed under product code of "JSM 840"), no change was found before and after the test. This fact indicates that the modified surface layers were bound so fast to the sheets as to defy separation.

Control 5

The same matrix sheets (ethylene-acrylic ester-maleic anhydride terpolymer) 200 μ m in thickness as used in Examples 12 to 14 were tested in the same manner as in Examples 12 to 14. The results are shown in Table 3.

The values of Δ resistance to friction were larger presumably because the oxide layers in the uppermost surface parts of the sheets were scraped by friction between adjoining surfaces.

EXAMPLE 15

A block copolymer composed of DMAA and GMA at a ratio of 2.8:1 was synthesized by following the procedure of Example 12. This block copolymer was deposited fast on a sheet (200 μ m) of an ethylene-acrylic ester-maleic anhydride terpolymer (produced by Sumika CDF Kagaku K.K. and marketed under trademark designation of "Bondine TX8030") in the same manner as in Examples 12 to 14 and was tested in the

same manner as in Examples 12 to 14. The results are shown in Table 3.

EXAMPLE 16

An ethylene-acrylic ester-maleic anhydride terpolymer (produced by Sumika-CDF Kagaku K.K. and marketed under trademark designation of "Bondine TX8030") and polyethylene were blended at a ratio of 1:1 and the resultant blend was manufactured into a catheter tube measuring 3 mm in inside diameter and 4 mm in outside diameter. The same THF 5% block copolymer solution (containing 1% by weight of pyridine) as used in Example 12 was injected into the tube by the use of a syringe pump, left standing in the tube at normal room temperature for 30 seconds, and discharged from the tube. Then, the tube was treated in an oven at 80° C. for 18 hours, washed with water, dried, and cut open with a knife to expose the interior surface thereof, left to be hit by dripping water, and tested for lubricity. It was found to have formed a ropy surface offering only low resistance to friction.

EXAMPLE 17

An X-ray contrast catheter (3.6 mm in outside diameter) was produced with a blend of an ethylene-acrylic ester-maleic anhydride terpolymer (produced by Sumika-CDF Kagaku K.K. and marketed under trademark designation of "Bondine AX8390") with 50% by weight of tungsten as a sensitizer. This tube was left immersed in a THF solution (containing 1% by weight of pyridine) containing the block copolymer of Example 13 at a concentration of 2% at normal room temperature for three seconds, dried, and heated for reaction in an oven at 60° C. for 40 hours. The tube was then washed with water, dried, and then left to be hit by dripping water to determine lubricity. It was consequently found to have formed a ropy surface offering only low resistance to friction. After it had been forcibly rubbed 20 times with a finger tip, it still retained lubricity intact.

EXAMPLE 18

A catheter 3 mm in inside diameter and 4 mm in outside diameter was produced with a material obtained by blending an ethylene-acrylic ester-maleic anhydride terpolymer (produced by Sumika-CDF Kagaku K.K. and marketed under trademark designation of "Bondine TX8030") and polyethylene at a ratio of 1:1. This tube was kept immersed in a solution of THF (containing 1% by weight of triethyl amine) containing the block polymer of Example 12 at a concentration of 2% by weight and further containing 0.1% of hexamethylene diamine as a cross-linking agent at normal room temperature for 30 seconds and then heated for reaction in an oven at 80° C. for 18 hours. When this tube was immersed in a physiological saline solution and rubbed with a finger tip, it was found to have formed a low-friction surface highly slippery as compared with an untreated tube.

TABLE 3

| | Value of resistance to final friction | Δ value of resistance to friction |
|------------|--|---|
| Example 12 | 62 gf | 10 gf max. |
| Example 13 | 72 gf | 10 gf max. |
| Example 14 | 70 gf | 10 gf max. |
| Control 5 | 443 gf | 72 gf |
| Example 15 | 172 gf | 10 gf max. |

What is claimed is:

1. A medical tool comprising:

a water-swellaible polymer comprising a moiety manifesting lubricity and another moiety having a first reactive functional group selected from the group consisting of an epoxy group, an acid halide group, and an isocyanate group in the molecular unit thereof; and

a material, chemically bonded to said water-swellaible polymer by means of a proton-donating group of said material, capable of reacting with said first reactive functional group, said proton-donating group selected from the group consisting of an amino group, an imino group, a hydroxy group, a carboxyl group, a mercapto group, or mixtures thereof;

said medical tool exhibiting lubricity in a wetted state.

2. The medical tool according to claim 1, wherein said first moiety is derived from at least one hydrophilic monomer selected from the group consisting of dimethyl acrylamide and maleic anhydride.

3. The medical tool according to claim 1, wherein said second moiety is derived from at least one monomer selected from the group consisting of glycidyl methacrylate, methacrylic acid chloride, methacryloyloxy ethyl isocyanate, and glycidyl acrylate.

4. The medical tool according to claim 1, wherein said water-swellaible polymer contains at least one copolymer selected from the group consisting of a block copolymer and a graft copolymer.

5. The medical tool according to claim 4, wherein said copolymer is a block copolymer.

6. The medical tool according to claim 5, wherein said block copolymer comprises glycidyl methacrylate and dimethyl acrylamide.

7. The medical tool according to claim 1, wherein said material is at least one member selected from the group consisting of a modified polyolefin, polyether, polyurethane, polyamide, polyimide and nylon.

8. The medical tool according to claim 7, wherein said modified polyolefin is a polyolefin modified with methacrylic acid.

9. The medical tool according to claim 1, wherein said proton-donating group is a carboxyl group.

10. A medical tool according to claim 1, which is a catheter.

11. A medical tool comprising:

a water-swellaible polymer comprising a moiety manifesting lubricity and another moiety having a reactive functional group selected from the group consisting of a hydroxy group, an amino group, and an epoxy group in the molecular unit thereof; and a material chemically bonded to said water-swellaible polymer by means of an acid anhydride group of said material capable of reacting with said reactive functional group;

said medical tool exhibiting lubricity in a wetted state.

12. The medical tool according to claim 11, wherein said moiety manifesting lubricity is derived from at least one hydrophilic monomer selected from the group consisting of dimethyl acrylamide, acrylamide, vinyl pyrrolidone, and vinyl ether.

13. The medical tool according to claim 11, wherein said another moiety is derived from glycidyl methacrylate.

14. The medical tool according to claim 11, wherein said water-swellaible polymer contains at least one copolymer selected from the group consisting of a block copolymer and a graft copolymer.

15. The medical tool according to claim 14, wherein said copolymer is a block copolymer.

16. The medical tool according to claim 15, wherein said block copolymer comprises glycidyl methacrylate and dimethyl acrylamide.

17. The medical tool according to claim 11, wherein said acid anhydride is maleic anhydride.

18. The medical tool according to claim 11, which is a catheter.

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